Massive Class as a Naval-Structural Material

A Report of the

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MASSIVE GLASS AS A NAVAL-STRUCTURAL MATERIAL

REPORT OF THE COMMITTEE ON MASSIVE GLASS AS A NAVAL-STRUCTURAL MATERIAL

NATIONAL MATERIALS ADVISORY BOARD
Division of Engineering - National Research Council

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Edwin Myskowski Chairman, National Materials Advisory Board Ad Hoc Committee on Massive Glass as a Naval Structural Material

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ABSTRACT

Massive glass has potential as a structural material for a variety of high efficiency, deep ocean applications. However, neither the existing data on massive glass nor current industrial production capability are adequate for the task. This is especially true in producing a man-rated glass pressure hull by a target date of 1930.

The application of glass as a structural material for deep submergence has been reviewed and evaluated in this report. Specific areas of glass technology requiring research, development, testing and evaluation effort are described. A structural design scale-up program using models and full-size pressure hulls is suggested. Concurrent materials studies, design evaluation programs, and production development are recommended.

I. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are the most salient reached by the Committee:

General Conclusions

- 1. Monolithic glass and glass-ceramic materials have attractive mechanical and physical properties that make them realistic candidate materials for advanced high-performance naval structural applications.
- 2. At present, our knowledge of glass materials and their engineering design specifications for translation into practice for such high-performance applications as deep-submergence structural applications is inadequate.
- 3. To exploit fully the potential of these glassy materials for such applications, it will be necessary to complete several diverse engineering-oriented research and development programs within the next 10 years (1970-1980).
- 4. If such programs as those recommended in this report are implemented on a priority basis, glass will be usable as a structural material in a variety of deep-submergence applications by 1980, including its possible use as a man-rated vehicle-hull material.
- 5. At present, the industrial capability for production of thick massive glass shapes required for deep-submersible hulls does not exist.

In view of these broad generic-type conclusions, a twofold approach to the problem is required at this time to develop fully the potential of glass as a structural material for deep-submergence applications.

(1) The guaranteed allowable engineering-design properties of candidate glass compositions must be established and joint design details evolved through

an engineering model and scale-up program. This program would include an evaluation of the performance of full-scale massive glass structures. (2)

A production technology must be developed to assure reliable, reproducible, structural glass components.

In the execution of such a program, the following specific conclusions and findings of this committee should be kept in mind:

- . Chemically surface-strengthened glasses and glass ceramics are far superior to annealed glasses for structural applications.
- No one design concept is clearly superior to all others at this time. Several designs merit further study and scale-up in a program aimed at construction of a man-rated vehicle.
 - Glass-to-glass and glass-to-metal interface interactions are not fully understood and require additional study.
- Realistic specifications must be developed for sections of massive glass. The industry must demonstrate a capability of fabricating massive glass sections of reproducible quality.
 - All harmful defects in glass cannot, at this point, be defined.

 All discernible defects must be studied, defined, and characterized to establish criticality and related acceptance criteria.

 Nondestructive testing techniques must be improved to assure detection of all critical flaws in structural compenents and assemblies.
 - Impact, cyclic, and long-term static-loading effects on glass and glass structures must be studied and useful limits established.
- Improvements are needed in surface-strengthening processes for glasses, including increased case depth on large, multicurved, thick-walled shells.

Optimization of glasses with "tailered" physical and mechanical properties should be explored to realize fully the potential of glass as a structural material.

Recommendations

In view of the above, the Committee recommends the following specific course of research and development action:

- 1. A program to develop production capability for large, thick, glass shapes should be initiated. Typical shapes would include hemispheres, spherical segments, and a full sphere with a hatch opening. The objective of this program would be to develop an industrial capability to melt, process, fabricate, and handle massive glass shapes with the reproducibility and quality levels needed for certified, man-rated vehicles.
- 2. Optimum design of joint configurations and optimization of material surface treatments should be accomplished promptly. Since most of the failures in glass structures originate at a surface, design engineering and process/materials development should be focused primarily on the highly loaded edge and in the region adjacent thereto.
- 3. Design specifications must be established. This will require selection of relevant test procedures and careful accumulation of data from realistic specimens. Effects of impact, cyclic, and long-term static loading must be included, and reliable performance of large-scale models should be demonstrated under these conditions of loading.
- 4. Studies of several promising design concepts using currently available glass and glass-ceramic compositions should be started early in the program.
 - 5. Development programs to improve the quality and depth of

chemical surface-strengthening layers will raise the reliability of glass structures. The attainment of the high levels of reliability required for man-rated vehicles must be demonstrated. A 0.100 inch-thick surface compressive layer is set as a development target.

- 6. Improved methods of nondestructive testing should be developed to assure product quality. For example, development of continuous monitoring devices capable of detecting incipient damage in the structure should be included.
- 7. New glass compositions should be developed to optimize glass deep-submergence vehicles. Among the target requirements of these new compositions is that to match elastic and physical properties to those of companion metal structural elements.

II. INTRODUCTION

In today's rapidly advancing technology, design concepts and operational hardware are limited largely by the properties and performance of available materials. Most of the progress is made in small increments as a result of gradual improvements in the properties and the understanding of the materials used. There is a natural tendency to use materials that are familiar and whose reliability has been proven; this is both understandable and commendable since failure of a component or vehicle could endanger human life.

However, the resistance to consideration of materials in applications that may be new for a specific material is sometimes based on emotional factors. History is replete with examples of such resistance, whether it was the change from wooden sailing ships to steam-driven ironclads, or the more recent change from the HY 80 grades of steel to higher-strength steels in submarine-hull construction. Unless a new candidate material is adequately evaluated for its applicability in accordance with a properly programmed plan, the protagonists will polarize into irreconcilable factions, with the proponents willing to take unnecessary risks while the opponents completely close their minds to the potential of the material under consideration. Such a situation benefits no one: it is wasteful of time and money and delays technological progress. On the other hand, a realistic assessment of a new candidate material and the problems that must be resolved before it can be used with confidence will provide a base on which the material will find its area of useful application.

Glass is an ancient material with a long history of use by man. It is widely applied in optics, containers, and decorative artifacts, but structural applications have been limited. This is due to the fact that glass

is weak in tension and fails in many situations because it is brittle. However, brittleness and low tensile strength do not automatically disqualify a material for structural usefulness. By operating within the constraints imposed by the physical and mechanical properties of other brittle materials such as stone, brick, and concrete many structures have been designed and built, and have endured for long periods.

Apart from their brittleness and low tensile strength, glasses have very attractive properties such as low density, high compressive strength, modulus of elasticity comparable to engineering metals, and good resistance to attack by a wide variety of corrosive environments. Analytical studies have shown that if glass can be used at high stress levels (10⁵ psi) in deep-submergence pressure hulls, a very low weight-to-displacement ratio could result.

In addition, glass and glass-ceramic materials possess some unique characteristics that may be advantageous for naval structures. The transparency of glass, for example, not only makes it valuable for use in manned vehicles when viewing of the environment simplifies piloting and observation, but also permits optical inspection for inherent flaws and induced damage in the finished part.

Committee Scope, Objective, and Rationale

With the above as background, the Office of the Director of Defense Research and Enginering of the Department of Defense requested in January 1969, that the National Materials Advisory Board of the National Academy of Sciences-National Research Council-National Academy of Engineering establish an ad hoc Committee on (the Engineering Aspects of) Massive Glass as a Naval Structural Material.

Accordingly, this committee was charged with studying the technological potentials and limitations of massive glass in order to identify the roadblocks and opportunities for using such materials in naval structures, especially deep-submergence pressure hulls.

Early in its work and in order to establish a realistic goal, the Committee determined the Navy's specific range of areas of potential interest. One of these was for a target vehicle, defined essentially as a Deep-Submergence Search Vehicle (DSSV) type, with an operational capability of 20,000 feet, a hull weight-to displacement ratio not exceeding 0.5, and a service life of 10 years with 2,000 excursions to operational depth.

Such submergence vehicles are being designed and built for an operational depth of 20,000 feet. However, these vehicles have non-buoyant pressure hulls made of high-strength steel and must use external syntactic cellular flotation material to obtain the required positive buoyancy. Similar vehicles with glass pressure hulls would have a potential for greater payload and operational capability without the use of auxiliary means of flotation or other external material required for positive buoyancy (syntactic cellular material, hard tanks, etc.).

In assessing the application of glass for vehicle pressure hulls as well as for other deep ocean structural uses, the Committee examined the properties and performance of some commercially available candidate glass and glass-ceramic compositions to evaluate both the attractive features and the limitations of these materials. Existing test methods were studied to determine their adequacy. An effort was made to evaluate existing industrial capability for the production of massive glass sections and to define the additional capability required. Critical design areas such as interfaces and penetrations requiring special emphasis were noted. The study was targeted toward developing a technology capable of producing a man-rated glass

submersible within 10 years from the start of such a project. Its specific goal is the production of a high-structural-efficiency deep submersible for which glass would provide special advantages.

No cost estimate has been made for such a program because a number of factors will determine the ultimate cost. These factors include determination of the total number of vehicles to be fabricated and tested, the annual production rate of full-scale vehicles, and the philosophy on which certification is to be based. Without a firm commitment to the need for such a vehicle, a cost estimate would be either misleading or meaningless.

In summary, the Committee report (1) presents a review of the current technology for application of glass for naval structures; (2) identifies areas in which research and development work is required to ensure the availability within 10 years of glass components suitable for structural applications and made to realistic specifications; (3) recommends development of production equipment and fabrication technology for making massive-glass components; and (4) sets forth an approach to the solution of design and fabrication problems of man-size massive-glass pressure hulls. The report also recommends early use of glass in unmanned structural applications to accumulate the engineering, fabrication, and operational experience needed to expedite certification of the glass for man-rated submersibles.

III. REVIEW OF THE STATE OF THE ART

This section of the report reviews some characteristics of glass and some of the experimental work done to evaluate glass as a naval-structural material. It is intended to provide background and perspective; it is not comprehensive.

Glass Technology

During the time that glass has been used for utilitarian tasks, many tests have been conducted to determine its properties. The degree of relevancy of the tests and the degree of control of test conditions have varied, and the usefulness of the strength data for engineering design is questionable. The reported values of tensile strength vary from a few hundred to several hundred thousand psi, depending on the flaw types, sizes, and populations in the test specimens and on the test conditions. Typical design allowables in tension for annealed glass, thermally tempered glass, and chemically strengthened glass are 1,000, 4,000, and 10,000 psi respectively. However, for severe structural service, tensile stresses in glass should be avoided.

On the other hand, glass has very high compressive strength. While considerable scatter occurs in data from compression tests, the average compressive strength of glass is very much higher than its apparent tensile strength, with values falling between 100 and 600 thousand psi in carefully conducted tests. The effect of surface flaws and internal defects is not as severe when the glass is loaded compressively. In fact, it is difficult to make glass fail in compression; failure is usually due to some tensile component of the applied load. Surface flaws, no matter how minute, are the most likely sites of initial failure; they then propagate through the section to produce failure in the member. The effects of internal defects are generally not as critical, although "stones" are a major problem.

Glass as a Hydrospace-Structural Material

As the technology of glass has advanced, the feasibility of its use as a structural material for deep-submergence applications has become more evident. Investigation of efficient pressure-resistant structures of glass for applications in deep-submergence vehicles and equipment started sometime in 1961 at the Naval Ordnance Laboratory (1a) (NOL) in White Oak, Maryland, at the David Taylor Model Basin, (1b) now the Naval Ship Research and Development Center (NSRDC) at Carderock, Maryland, and at the Ordnance Research Laboratory (1c) at State College, Pennsylvania.

Development Funds and partly from the Special Projects Office, Deep Submergence System Program (NSP) and later from the Deep Ocean Technology Project), a viable technology has been developed for glass as a hydrospace-structural material. Most of the experimental work has been done at NOL and NSRDC, NOL's work being both in the laboratory and in the deep ocean. The Naval Research Laboratory and the National Bureau of Standards have done supporting work, generally of a fundamental nature. The Naval Undersea Research and Development Centers at San Diego (2a) and at Hawaii, and the Naval Civil Engineering Laboratory at Port Hueneme, California, have concentrated on building state-of-the-art hardware. Commercial and scientific applications for pressure-resistant glass instrument cases and other structural applications have been explored to some extent.

The work has been far-ranging in scope and sometimes quite intensive. It includes static, cyclic, and dynamic structural tests on spheres, studies of the sensitivity of glass to corrosion or marine biological attack, development of test methods and nondestructive testing procedures, demonstration of the increased ability to tolerate shock loading at great depths in

the ocean, analytical and experimental investigations of the joint problem, evaluation of design concepts and fabrication methods, attempts to increase the depth of the "case" or layer of surface compression by electrochemical diffusion, and investigation of plastic cladding for greater impact protection. In a few instances the work has been completed; in most cases it has been carried far enough to delineate the problem and to outline a probable method of approach, leaving a large amount of work to be done.

Most of the work has been done on annealed glass, not because annealed glass, especially for manned structures, is advocated, but because structural elements of annealed glass are sometimes available from stock and otherwise are usually available on order, especially the larger items. Surface compressed-glass structures usually are available only with long lead times. Forming and processing of surface compressed glass have been demonstrated only on relatively small parts.

Small Glass Test Elements

Most of the work has been done on relatively small parts, usually 10-inch-diameter spheres. Corning Glass Works (CGW) has produced many fusion-sealed spheres of borosilicate glass (CGW Code 7740) with outer diameters ranging to 16 inches. Thickness to radius (t/r) ratios were usually 0.05 (0.07 in a few instances). With a nominal deviation of 5 percent in local radius, Krenzke (3) places the average buckling pressure at 19,000 psi for this ratio. (The maximum ocean depth of 36,000 feet provides a pressure of 16,000 psi, and a depth of 20,000 feet, which encompasses 98 percent of the ocean floor, provides a pressure of 8,900 psi.)

A generally good experience with fusion-sealed floats (for example, five 10-inch-diameter borosilicate glass spheres have been pressure-cycled to 10⁴ psig -- 10⁵ psi wall stress -- over 5,000 times with

no discernible degradation) led to the next stage in the program: a container allowing ready access. Initially, this was accomplished by grinding a flat edge on the equator of each hemisphere, thus providing planar surfaces for mating the hemispheres at the common equator. Stop-cock grease was used to lubricate these bearing surfaces, and hose clamps were used to hold the two units together with a slight prestress at sea-level pressure. This approach with annealed glass was very disappointing as failures occurred at hydrostatic pressures well below 10⁴ psig. At 5,000 psig, cycling produced failures in about 20 excursions. Failures were explained on the basis of mating-surface discontinuities and stress risers caused by grinding. As the uniform external pressure was changed, differential movement between the two hemispheres and Hertzian stresses produced local tensile stresses that were greater than the coincident local compression-stress component due to hydrostatic loading. Thus the cracks that appeared perpendicular to the ground faces, and within the walls of the spheres, were explained. (It should be noted that most instances of reported failures were not catastrophic; failure was reported when any cracks appeared or grew, almost invariably at the equator, illustrating the importance of solving the joint problem.)

Joints

Much of the subsequent work has been an attempt to solve the joint problem. First aluminum and later titanium members were joined to the equatorial edges of hemispheres, with the actual closing of the sphere involving a metal-metal juncture. Water-tightness was achieved by using grease or epoxy resin at the glass-metal interface and elastomeric O-rings or gaskets at the metal-metal interface. Failures continued to appear in the "plane" of the sphere, perpendicular to the equatorial edge, and were attributed to tensile stresses generated due to elastic effects, differential motion and/or hydrostatic pressures generated by flowing grease, seawater,

or metal.

surface compressed glass so that tensile forces generated at the bearing surface must first overcome the surface compression forces built into the glass. (Two Corning Code 0315 glass hemispheres, strengthened by ion-exchange, mated at ground surfaces [ground before ion-exchange] withstood 100 cycles to 10⁴ psig.) The second solution is to form a half-toroidal contact surface on each hemisphere, with the radius of the toroid being half the thickness of the hemisphere. The hemispheres are then nested in mating concave grooves in the metal-mating pieces. Units of this type with aluminum alloy have been cycled several hundred times to 10⁴ psig. Models combining both concepts -- chemically strengthened glass hemispheres with toroidal edges mated into grooved titanium joint rings -- withstood 10,000 cycles to 8,900 psig (20,000 feet) and multiple cycles to 13,500 psig. A variety of other approaches are also under consideration. (5, 3)

Massive-Glass Parts

The results of a relatively few tests on large spheres -
44.5 and 56 inches in diameter -- have not been as encouraging as those obtained on 10-inch-diameter spheres. Two 44-inch-diameter fusion-sealed borosilicate spheres tested at NSRDC failed at 3,500 and 4,500 psig; in both cases failure occurred in the fusion-sealed seam because of structural discontinuities in the seam. A similar sphere immersed in the ocean by the Woods Hole Oceanographic Institution imploded at 7,800 feet (3,450 psig). Three 44.5-inch hemispheres tested at Southwest Research Institute have all failed at less than 3,500 psi, with cracks at or near the glass-metal interface. In the latter cases the causes of failure cannot be attributed to poor fusion seals; failures were probably due to poor geometric control of wall thickness

or sphericity or to defects in the glass (see the discussion on quality later in this section). A 56-inch OD borcsilicate hemisphere intended for the HIKINO program at the Naval Undersea Center in Hawaii reportedly failed by spalling at the interface after 15 cycles to 1,100 psig. In this instance, the joint design involved the half-toroidal radiused parts with an epoxy coating on the metal. The possibility exists that a parting agent was ineffective in preventing epoxy sticking to the glass, and a phenomenon known as "glue-chipping" was responsible for the spalling.

Glass-Ceramic Submersibles and Vehicles

A glass ceramic (CGW Code 9606) has been used in three programs of note:

- . <u>Benthos.</u> This vehicle, about 100 inches long and 12.5 inches in diameter, was evaluated by the Ordnance Research Laboratory at Pennsylvania State University. Cylindrical sections of the Benthos contained integral rib-stiffeners. Five separate 20-inch-long sections of glass ceramic were joined axially in this design. Failures occurred by chipping and splitting at the joints.
- Lockheed Bisphere Test Model. Glass-ceramic end caps for the composite glass and titanium bisphere test model (built by the Lockheed Missiles and Space Co.) consisted of two machined hemispheres of 15-inch diameter with half-inch thick walls (a t/r of 0.067). All surfaces were ground to finished contours. The interface with the flat TMCA ticanium alloy (6-2-1) midbody was sealed with a gasket of nylon fabric reinforced elastomer (duPont Fairprene). Two sets of hemispheres were tested. Cracking at the joints observed after 495 cycles to 8,900 psi (20,000 feet) in the first set was sufficiently extensive to justify test termination. After installation of two new glass-ceramic hemispheres, the bisphere testing was continued until

catastrophic failure occurred after 80 cycles to 8,900 psi (69,000 psi wall stress).

submersible is a glass-ceramic/titanium-segmented 18-inch-diameter sphere. Glass-ceramic (CGW Code 9606) pentagons were cast and then machined to pentagonal-spherical segments of 0.400-inch thickness (t/r = 0.044). Each is a size that can be circumscribed by a 5-inch-diameter circle. Recently this model was subjected to a uniform external pressure of 5,400 psi (average membrane stress of 120,000 psi). It has not been subjected to cyclic loading.

Quality

The generally poor performance of the massive-glass parts in contrast to the smaller parts is easily understood when the quality levels are compared. The large hemispheres were formed simply to demonstrate that fabrication of large parts was feasible. Furthermore, the borosilicate glass used is difficult to melt in good quality. As a consequence, the large pressed hemispheres had a high defect level, with huge blisters, chill wrinkles, and large stones throughout the parts. In addition, dimensional control was extremely poor, as shown below:

DIMENSIONAL CONTROL OF IARGE PRESSED HEMISPHERES

	44.5-inch Hemispheres	56-inch Hemispheres
Number of specimens	40	8
OD range	$44^{1/8}$ to $44^{3/4}$ in.	$56^{1/8}$ to $56\frac{1}{2}$ in.
Height range	$20^{5/8}$ to 23 in.	$28^{3/8}$ to $28^{5/8}$ in.
Wall thickness:		
Rim	$\frac{1}{2}$ to $2^{5/16}$ in.	$1^{1/4}$ to $2^{1/8}$ in.
Pole	0.85 to 2.23 in.	1.33 to 2.33 in.
Midplane	0.94 to 3.06 in.	1.68 to 1.97 in.

The quality level for the borosilicate (CGW Code 7740)
hemispheres of 8-, 10-, and 16-inch diameter was much better than for the
larger parts. The acceptable quality can be described as follows:

Blisters -	open blisters rejected. Buried blisters up to 3/16-inch diameter for wall thickness less than 0.300-inch and up to 1/4 inch diameter for thicker walls.
Chips and Checks -	all degrees rejected.
Contaminated Edge -	all degrees visible to the unaided eye under normal lighting rejected.
Pits -	Four 3/32-inch round, or equivalent area, by 1/32-inch deep per hemisphere permitted. Pits less than 0.620-inch round are disregarded.
Scale -	all film scale accepted. Surface scale disregarded to 0.020-inch in greatest dimension - acceptable up to 1/16-inch in greatest dimension on either surface.
Scratches -	individual scratches over 2.5 inches in length unacceptable. Total length of all scratches not to exceed 15 inches.
Shear Marks -	inside surfaces must be smooth.
Stones -	all surface or checked stones are cause for rejection. Hard-buried stones up to 1/16-inch greatest dimension and flaky-

buried stones up to 1/8-inch greatest

dimension were considered acceptable.

Joining Defects -

the equatorial joint quality of fusionsealed spheres (two joined hemispheres) can be described as follows:

- OD intruded seal unacceptable. Smooth extruded bead up to 1/16 inch acceptable.

 Sharp discontinuities not permitted.
- ID indentations of seal beyond nominal internal radius not acceptable. Build-up acceptable if no sharp discontinuities exist.

Dimensional control of the small pressed borosilicate (CGW Code 7740) hemispheres was also better than for the large hemispheres. An attempt was made to hold the ΩD to $\pm 1/8$ inch and wall-thickness variations to loss than 10 percent. A representative sample from a batch of thirty-five 8-inch sealed spheres had a maximum runout variation of 0.075 inch and a minimum runout variation of 0.008 inch; the average of the variation of all the 35 spheres was 6.025 inch. For a sample of twenty-six 10-inch diameter spheres, the comparable values were 0.084 inch, 0.010 inch, and 0.025 inch.

The quality of the surface compressed glasses supplied was better than for the borosilicates, and the quality of the glass ceramic was atill better (rated very good). The sag-formed soda-lime hemispheres supplied by PPG Industries are also of very good quality.

IV. DISCUSSION

A. GLASS TECHNOLOGY

Physical Properties and Quality Considerations

Glasses and glass ceramics offer a wide range of physical properties. The table below indicates the range offered by commercially available compositions:

	Glasses	Glass Ceramics
Modulus of Rupture (psi) (transverse, abraded)	4,000 - 80,000	10,000 - 130,000
Young's Modulus, 10 ⁶ psi	7 - 14	10 - 20
Poisson's Ratio	0.15 - 0.28	0.20 - 0.27
Thermal Expansion Coefficient ppm/°C.	0 - 15	0 - 12
Density, gm/cm ³	2.1 - 2.5	2.5 - 2.7
Luminous Transmittance (% in 1 cm)	0 - 90	0-60

No single glass or glass ceramic commercially available today provides optimum material properties from an ideal design standpoint.

Additional research and development efforts can be expected to yield one or more specific compositions that will improve performance and have good melting characteristics and higher quality. Trade-offs and compromises will have to be made between various specific characteristics in any selected material.

The following requirements can be set down as goals for a glass or glass ceramic in massive sections for use as a naval-structural material.

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Material Properties

- (a) High compressive working strength (>100, 000 pεi) and tensile strength (>25, 000 psi).
- (b) Elastic constants (Young's modulus and Poisson's ratio) that are compatible with those of the metal selected for coupling at joints.
- (c) Low thermal expansion for ease of residual stress reduction in manufacturing and for low temporary stresses both in processing and in end use. Thermal expansion matching to metals at joints will be an important consideration, particularly for annealed glass.
- (d) High transparency and minimal light scattering for visibility and inspection.
- (e) Low density for optimum buoyancy.
- (f) Adequate chemical durability for sea environment.

Product Requirements

The composition should be of a type that can be melted in a large individual mass (volume) and is amenable to quantity production. Following melting, forming, heat-treating, and finishing, the final product should:

- (a) Exhibit high compositional and structural uniformity.
- (b) Contain no internal checks and a minimum number of crystalline inclusions, voids, and cords. Glass of optical quality would be ideal.
- (c) Surface checks should be limited to a very shallow depth.

Melting quality is of utmost importance. Much of the glass tested to date has not been of high quality. Even so, some performances have been encouraging. Until data are available that accurately spell out what defects are permissible, the only safe course is to strive for the highest quality possible approaching optical grade. A stone, for instance, may be viewed as a possible stress riser in compression or tension, and size does not necessarily alter its severity. Defects of this type cannot be specified at a zero level for practical manufacturing, but they should be held at a minimum in quantity and size.

Design Considerations

Design strength is the prime problem. Intrinsic compressive strength of glass is very high but engineering design allowables have not been established as they have for structural metals. Mechanical and chemical interaction with metal members incorporated at joints must be determined and controlled. Tensile strength is another matter. Modulus-of-rupture tests of glass cane and plate characteristically have disturbingly wide data spreads, usually attributed to large variations in types and distributions of surface flaws. When considering the large surface areas that hull sections will have, it is obvious that the chance of a serious flaw existing somewhere on the surface is very high. This argues for surface strengthening, like ion-exchange, that will pre-compress the surface layers to a depth that exceeds that of all likely flaws. Many individuals have studied the situation and feel that a "deep-case" pre-stressed glass or glass ceramic offers the only course to increase reliability for man-rated deep-submersible considerations.

Elastic behavior is another property that must be investigated thoroughly. It can be assumed for practical engir eering purposes that glasses

or glass ceramics are completely brittle (i.e., there is no permanent strain after removal of a stress). Eul and Woods (7) reported some nonrecoverable strain for these materials in shear, but more recent work by them indicates that the earlier work is doubtful and that no permanent strain exists.

Phillips ⁽⁸⁾ has developed empirical equations that relate composition to modulus. Recently he has extended this work to Poisson's ratio as well (see Appendix). The work of Phillips ⁽⁸⁾ should prove particularly helpful in developing glass compositions with specified values of Young's moduli for joint matching to metals.

Simple elastic behavior is readily handled by standard procedures. Elastic after-effects must also be considered. Unfortunately, little data are available. Furthermore, there is some uncertainty as to how to factor such effects into stress analysis.

Many mixed-alkali glasses are known to be dimensionally unstable near room temperature. Hagy and Ritland (9) have shown that measurable time-dependent dimensional changes persist in these glasses to temperatures as low as 100 °C, with indications that these effects continue to even lower temperatures. Evidence suggests very convincingly that these effects are caused by alkali-ionic migration, and that the magnitudes are much greater for mixed-alkali glasses than for single-alkali compositions. This phenomenon is responsible for ice-point depression in thermometers. The Jena normal thermometer glass developed in 1885 to minimize ice-point depression is a single-alkali glass.

There may be an association between these low-temperature microstructural instabilities and elastic after-effects. Murgatroyd and Sykes ⁽¹⁰⁾have shown that the delayed after-effect for a soda-lime glass is a factor of 10 higher than that for vitreous silica. Another composition, containing two alkalis, had a smaller effect than the soda-lime (single alkali),

which is not in keeping with the statement in the paragraph above.

Chemically strengthened glasses obviously fall into the mixed-alkali family. Kerper, Scuderi, and Eimer (11) have already observed relatively high elastic after-effects for these glasses. This must be taken into account somehow in stress analyses. Furthermore, for joints, the elastic properties of the surface-exchanged layers must be defined. To date, nothing has been reported in the literature on this. Experimental techniques are needed. Therefore, it should be kept in mind that, although strengthened glasses offer promise related to strength, some questions that they present have not been answered as yet.

Quality Assurance and Nondestructive Methods of Evaluation

General

The term, "quality assurance," is defined as the "planned and systematic pattern of all actions necessary to provide adequate confidence that the product will perform satisfactorily in service." To provide quality assurance for the complete assembly of a deep-submergence vehicle, at least three sets of procedures are required:

- (a) A materials specification with adequate tests to assure that the specification is met and including property measurements on the material to provide the engineer with the data necessary for design purposes.
- (b) Process controls that describe procedures for the fabrication and assembly of the material into a usable item.
- (c) Nondestructive tests to assure that the finished product meets all specifications and will perform satisfactorily in service.

The specifications must set tolerable limits for inspection procedures to include items such as:

- (a) Type of Glass or Glass Ceramic
- (b) Chemical Composition
- (c) Physical Properties to be Determined
- (d) Finish and Dimensions
- (e) Surface Treatment and Coatings
- (f) Critical Flaw Types, Sizes, and Distribution
- (g) Method of Test for Each and Inspection Procedures

The materials specification will require specimens to be prepared in various forms for property measurements, i.e., rods, slabs, discs, hemispheres, hyperhemispheres, etc. Applicable shapes will be required for certain property determinations.

Test Methods for Material Specification

Types of Glass

- (a) Surface-Strengthened Glass
- (b) Glass Ceramics

Composition - to be verified by chemical analysis

Physical Properties - Test methods for the determination of physical properties, in many cases, require specimens of given dimensions, and it is necessary that a representative sample of the material be used for these measurements. Such measurements cannot be made by nondestructive methods on massive glass. Listed below are some of the properties that are of importance to the design engineer. An indication is given of a method of

measurement and the areas in which a method must be developed.

- (a) <u>Light Transmittance</u> For annealed polished specimens of the glasses and transparent glass ceramics, 1 cm-thick samples shall be prepared and the transmittance determined on a suitable commercial spectrophotometer. No detailed procedure has been written for these measurements, but transmittance measurements are a fairly routine procedure.
- (b) <u>Stress Birefringence</u> The stress-optical coefficient (Brewster's constant) shall be determined on a prepared sample of the glass. A uniaxial loading method has been described (13) for this measurement. A laser scattering method (14) is being investigated at the Naval Research Laboratory for the determination of residual strains in massive glass and for the determination of the stress profile in the surface-compressed layer in chemically strengthened glass.
- (c) <u>Homogeneity</u> The visual-inspection methods for voids, seeds, bubbles, inclusions, striae, blisters, chips and checks, scale, scratches, and shear marks that are used for optical glass (15, 16) should be adapted to the inspection of massive glass. Rosberry (17) has described procedures for the determination of homogeneity in optical materials, which with suitable modifications, should be useful in the inspection of massive glass. Techniques of edge lighting of hemispheres have been used at the Naval Ordnance Laboratory to observe inclusions and seeds. The detailed procedures used will depend on the specimen size and shape. Nondestructive test methods must be devised to provide 100-percent inspection to locate and evaluate the defects that may be found in massive glass.
- (d) Density This property may be determined with precision by a buoyancy method (18) on suitable specimens.
 - (e) <u>Elastic Properties</u> Young's Modulus, E₀, Shear Modulus,

- G_0 , and Poisson's Ratio, μ_0 , shall be determined by ASTM Designation C623-69T. With a suitable cryogenic chamber and furnace, these measurements may be extended both below and above room temperature. This is a resonance technique and gives values of the short-time elastic constants. Specimens of specified dimensions are required.
- (f) Thermal Expansion This property should be measured on suitably prepared samples using ASTM Designation E228-66aT. (20) The temperature range normally reported for glasses is from 0 to 300°C, but a lower range is much preferred (for example, -50° to 50°C).
- (g) Refractive Index Various types of refractometers are available to measure refractive index, any one of which may be used. Values to ± 0.00005 may be obtained from a v-block refractometer on sawed samples, on which polishing is not required.
- (h) Delayed Elastic Properties In order to determine the response of structures to gradually changing and to static loads, data on the delayed elastic properties, relaxed Young's Modulus, \mathbf{E}_{∞} , relaxation time(s) of Young's Modulus, and relaxed Poisson's Ratio, μ_{∞} , are needed. Suitable methods for making these measurements are not now available, although shear-wave techniques appear promising. These methods also appear to offer a means of determining the clastic properties of the surface-exchanged layer which are important in the joint-matching problem. This is an area in which a measurement method must be developed.
- (i) <u>Modulus of Rupture</u> Measurements are desired under multiaxial loading stresses for surface-compressed glasses. Test methods are now under investigation but a standard procedure is not available. A concentricring method of loading to eliminate edge effects appears promising and is being considered by ASTM Committee C14, Subcommittee IV, but further work is required to develop the method for practical use.

Process Controls

As indicated above, process controls describe those procedures for the finishing and assembling of the massive glass into a usable item. The actual methods used will depend on the engineering specifications developed for items such as:

- (a) Grinding and polishing procedures
- (b) Chemical etching procedures
- (c) Mechanical tolerances and finishing
- (d) Surface treatment
- (e) Dimensional tolerances and inspection
- (f) Residual stress profiles and case depths in treated glass

 Control methods are required for these items and 100-percent inspection is required. Detailed records must be kept so that material traceability can be maintained through the complete manufacturing process.

Nondestructive Evaluation

Recently methods for nondestructive evaluation of materials have been examined by a National Materials Advisory Board committee. (21) In the preface to their report, it is pointed out that the ever-increasing demands of defense and space exploration have forced designers to attempt to exploit new materials and techniques with greater sophistication and efficiency in their design approaches. The net result has been the growth of an urgent need for more effective and more comprehensive approaches for nondestructive testing and evaluation. This certainly will be true in the case of massive glass as a naval-structural material.

Mondestructive methods applicable to massive glass are needed to detect and locate surface and internal flaws, and to determine whether the nonuniformities in physical properties are within tolerable limits. A general discussion on nondestructive testing may be found in the literature. (22, 23)

Perhaps one of the most important questions concerning the use of massive glass as a naval-structural material is that concerning critical flaw size. During the meetings of the National Materials Advisory Board committees concerned with the use of massive glass as a naval-structural material, it has been pointed out that inspection techniques beyond those used for optical glass are necessary and must be developed and applied to massive glass. It also has been stated that it is necessary to identify critical flaws and to develop inspection techniques capable of finding them. The classification of flaws in glass has been discussed, and from a practical point of view it was stated that we can only deal with those that are detectable, and that there was little point in rejecting any flaw less than 0.001 to 0.003-inch deep.

It is suggested here that no meaningful method, equipment, or criteria can be established until we have clear answers to two fundamental questions:

- 1. Are internal flaws likely to be a serious problem or, on the contrary, except for gross internal defects, can we entirely focus our attention on surfaces and edges?
- 2. If edge and surface grinding and polishing are necessary, can we realistically hope to have a flaw distribution superior to, or even equal to, that on currently manufactured plate glass?

The first question is basic in deciding what to inspect, when, and where. A quality criterion equal or superior to that for optical glass is easy to write but will not be easy to meet for massive glass. Even if it could

be met, is it necessary? If the statements by Perry, Bersch, and others are correct, it certainly is necessary. But, at the very least, it would seem that the evidence should be reviewed very carefully and that dimensional or other criteria should be assigned to the voids, foreign inclusions, crystals, striae, and other defects that, in their opinion, cause premature breakage. If, in the past, there have been really gross defects in the samples that have been broken, it may be possible by better quality control to minimize their size and severity in the future. Primary attention might then again be focused on surfaces and edges. If, on the other hand, it can be shown that these internal defects were quite small, but still caused failure, the problem is much more difficult.

The second question is partly tied in with the first but also must be examined on its own. If the hull must be ground and polished, and if this can be done to no better than present plate-glass quality, it is realistic to expect some long-time failure at tensile stresses of 1, 200 psi without surface strengthening. Unless it can be shown that internal defects (in a tension field) can cause failure at stresses lower than this, then these surface defects will still be the controlling factor. Data from Mould and Southwick (24a) and from Shand (24b) suggest that a (an average failing) stress of 1,200 psi may correspond to a crack depth of about 0.010 inches. This is unrealistic, however, for chemically strengthened glass where the surface-compression layer may be only 0.005 to 0.010-inches thick. A more realistic rejection criterion for surface defects is that they be not more than 0.003-inches deep. These will be well within the range that the naked eye can see. It should be possible, at greater cost, to reduce this limit to 0.001 inches and then examine the surface under low magnification. First inspection should be made before strengthening because surface compression tends to close up such flaws and make them invisible.

Thus, an investigation will be required to determine what type, size, and location of flaws in massive glass lead to rejection. The consideration or the effects of surface flaws on the strength of glass makes a strong case for the use of surface-compressed glass in which the thickness of the compressed layer is greater than the depth of all allowable surface flaws.

Test Methods

In the following section, nondestructive methods of evaluation for massive glass are listed with an indication of their potential usefulness.

(a) Visual

(1) Optical Techniques - These may employ the unaided eye, the aided eye, or a light-sensitive detector. Variations of optical methods are useful in detecting surface flaws, determining crack depths, inspecting surface finishes, determining surface roughness, and inspecting for homogeneity and internal defects.

Since glass is usually transparent in the visible region, visual and optical methods of inspection are particularly attractive. Visual tests long have been used for the inspection of optical glass, and, as pointed out above, these methods, or variations of them, should be used for massive glass. (15,16)

Rosberry ⁽¹⁷⁾has described a procedure for the measurement of homogeneity of optical materials in the visible and near infrared. His procedure includes a simple visual test, an examination in polarized light, a shadowgraph test, and finally the determination of uniformity in refractive index by an interferometric technique. This procedure permits putting a numerical value on the homogeneity of optical materials, and in this respect is a very valuable contribution. Certain aspects of the procedure could

well be adopted for massive glass.

Polariscopic examination is a common method of determining the residual strain in annealed glass and the apparent temper in heat-strengthened glass. In chemically strengthened glass, the depth of the strengthened or surface-compressed layer is relatively thin compared with the body of the glass, making it difficult to obtain accurate values of the surface stress. In addition, the specimen must be examined in cross section, so that the method is not applicable to strengthened massive glass shapes on a nondestructive basis. Use of production-control samples processed with the production pieces should be considered.

Bateson et al. (14) have described a method of measuring the birefringence in thick sections of glass by light scattering using a laser source. Current work at the Naval Research Laboratory is seeking to adapt this technique to chemically strengthened glass.

A differential surface refractometer of the type developed by the Glass Research Laboratory, PPG Industries, has been used to determine the depth of the surface-compressed layer on strengthened glasses by Hara. (25) He reports that his results show that the stress-induced birefringence and the approximate thickness of the stressed layer can be measured by surface refractometry. Presumably, Hara worked with flat surfaces. If the technique can be adapted for use on curved surfaces, it will provide a nondestructive means of evaluating two parameters of great importance in this program. Work in this area is required to provide a reliable method for measuring the stress-induced birefringence and the thickness of the surface-compressed layer.

In general, visual nondestructive methods of evaluation must be adapted for application to massive glass.

- (2) Penetrant Methods These methods include the use of fluorescent liquids, gases, and charged particles to penetrate the surfaces of materials and to make surface cracks and flaws visible. They have not been applied to any great extent to glasses, but their potential should not be overlooked in the search for reliable methods to detect and assess surface flaws.
- brittle coatings are applied to surfaces of materials and are used to detect the magnitude and distribution of strain under load and to locate surface flaws. Again, these methods have been little used on glasses.

(b) <u>Holography</u> (21, 26, 27)

as a source, is imagery by wavefront reconstruction. The object is illuminated by coherent light and the light is reflected from the object or transmitted through a transparent object. This light falls on a photographic plate, as does coherent light from a reference beam. The photographic plate records light from every illuminated point of the object and the interference of this light with light from the reference beam. By recording on the same plate an image of the object in a free and then in a subsequently deformed state, a holographic interferogram is produced. Such an interferogram contains a comparison in terms of a contour fringe pattern that shows minute distortions occurring between exposures of the film. The technique makes practical a new type of interferometry for recording minute deformations, which is not dependent on precise optical equipment and alignment as is normally required.

For stress and vibration analyses, light holography promises to be as useful as a strain gage and as a detector of material surface deformations that precede failure. It should also be very useful in observing the deformation of materials under pressure. A recent publication (26) describes a system that yields high-quality holograms of objects several cubic meters

in volume. Coherent radiations in the ultraviolet and infrared, as well as in the visible, offer promise for holographic studies of material surfaces to determine uniformity of coatings, surface cleanliness, and to detect surface flaws and cracks. The wavelength differences available in coherent sources would provide sensitivities to different materials and surface layers because of their different reflection and transmission characteristics.

Holography is not necessarily limited to light. In principle, holography can be performed with any wave radiation such as the entire electromagnetic spectrum, and other forms of energy including ultrasound and neutrons. Many potential areas of usefulness can be imagined but such techniques must be developed.

(c) Penetrating Radiation

Radiography is used for flaw detection, and for voids and inclusions. A radioactive gas penetrant (28) is said to be effective in the detection of microscopic surface flaws that are not found with fluorescent dye penetrants. Detection may be either by photographic film or by electronic-scanning systems. Detectable concentrations of the gas are said to form in defects from about 10Å up.

(d) Mechanical Vibration (Sonic and Ultrasonic)

through transmission, and resonance techniques. They may be used to detect flaws, cracks, voids, and inclusions, and to determine the elastic properties and the thickness of surface layers. The acoustic propagation pattern is influenced by various factors, including sound-beam characteristics, boundary conditions of the material, attenuation, mode conversion, shape and contour of test specimen, testing frequency, and the like. With the possible exception of resonance techniques for measurement of elastic constants,

these methods are just beginning to be used to determine glass properties. This is an area in which work is needed to develop the full potential of such methods.

A Navy Research Laboratory report (29) has indicated that the elastic modulus of an ion-exchanged layer, 6 or 7 mils thick, on a strengthened glass ceramic can be measured by ultrasonic means. It remains to be seen how accurately such measurements can be made.

or sounds, and the study of structures under pressure should prove useful in their evaluation. Stress-wave analysis is being pursued by Naval Ships Research and Development Center. Such studies may indicate the initiation and propagation of cracks and the misalignment of joints. Generally, the range used for emission studies is 30 to 300 KHz. Again, work in this area is required to develop and realize the potential of these methods.

Quality and Nondestructive Recommendations

Quality assurance and nondestructive testing methods of evaluation are essential procedures that must be developed or refined and used to provide adequate confidence that massive glass will perform satisfactorily as a naval-structural material. Material specifications and process-control procedures must be developed at the same time to assure that the desired hardware is manufactured in a reproducible manner.

Specific recommendations, as indicated in the discussion above, are:

1. That a detailed materials specification* be written to procure

^{*} H. A. Perry of NOL has prepared a preliminary specification that is updated as additional information becomes available.

massive glass of the proper quality for use as a naval-structural material.

- 2. That process-control procedures be written to describe procedures for finishing the raw glass into the desired structures.
- 3. That methods be developed for the determination of:
 - (a) stress profile in strengthened glass,
 - (b) depth and elastic behavior effects of strengthened layer,
 - (c) the number, size, and location of surface flaws in glass,
 - (d) delayed elastic properties of glass, and
 - (e) modulus of rupture under multiaxial stress conditions.
- 4. Nondestructive methods of evaluation that appear to have potential for use on massive glass and that have not been developed, or whose development has not been completed are:
 - (a) laser-scattering technique for measuring birefringence and stress profile in massive glass,
 - (b) use of surface refractometer to measure surface compression and depth of strengthened layer in surface-compressed glass,
 - (c) use of holography to determine minute local distortions in massive glass under pressure, and
 - (d) use of ultrasonic and sonic methods to evaluate flaws, cracks, voids, and inclusions in massive glass and as a possible means of determining the thickness and elastic properties of the ion-exchanged layer of a massive glass component.

B. PRODUCTION OF MASSIVE GLASS

Introduction

While there is a vast amount of production know-how in the glass industry, comparatively little of it has been brought to bear on the problem of producing high-quality pieces of massive glass. As a result, there is relatively little existent facility capability.

Simply stated, the major problem for the glass-manufacturing industry is to form and anneal massive pieces of glass of composition suitable for surface strengthening, relatively free from stones, secus, blisters, and cords, and with combinations of elastic properties compatible with the properties of candidate companion metals. Dimensional accuracy suitable for use as formed, or after grinding and polishing, is required. Each piece must be maintained in nearly pristine condition by a suitable overlay protection to prevent degradation and surface damage.

Such pieces of glass may range from 7 to 10 feet in diameter, and weigh 1 to 5 tons, and have a finished thickness up to 6 inches.

Glass

Assuming that a suitable glass composition capable of adequate surface strengthening will be forthcoming from which massive-glass components can be produced, we can look at the subsequent problems of manufacture.

It is generally accepted that stones of any size, type, or location must be minimized in the glass for the 20,000-foot depth man-rated submersible.

Therefore, it seems logical that to help keep stones out of the finished hemisphere the following must be done:

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- 1. Composition should be such that lengthy heat-treating cycles could be tolerated without uncontrolled devitrification.
- 2. The glass to be delivered to the mold should not contact a material that is potentially stone-producing such as a ceramic crucible, but should be melted and handled only in suitable materials such as platinum.
- 3. Composition is such that it will melt easily and not leave unmelted batch stones. The batch should be finely divided and intimately mixed and prepared (wetted or pelletized) so that separation or dusting will not occur, and so that it will permit the use of optimum melting means.

Furnace

Following the assumption that the glass must be delivered to the mold from a furnace made of material that will not introduce stones (for example, a platinum-lined one), is it then practical to charge raw batch pellets and melt and fine each charge of glass, or should the glass be prepared in large quantities in continuous furnaces, which, because of size, would have to be constructed of more economical materials such as ceramics? If preparation of the base glass in relatively large continuous furnaces is required, it would be necessary to prevent delivering stones into the mold. This might be done by forming the glass into intermediate pieces that could be checked for quality and then used either to charge the platinum-lined pot furnace for remelting into the final charge for the mold, or introducing the intermediate glass pieces formed into the mold for melting, fusing, or other processing.

Such considerations will have to be investigated for practicality, and the method chosen could be dictated by the total production and the rate of production of massive-glass pieces required from a given facility.

Much is known by the industry about design, firing, instrumentation, and control of glass-making furnaces, and this know-how can be used to produce the needed furnaces once the production requirements are defined. While these furnaces for structural glass may be specialized and refined, it is thought that only a design and development program is required rather than any great amount of research. Such design certainly will be dictated in part, by the method of heating (gas, electric melting, electric boosting, etc.), which, in turn, will take into account the form of batch material (dry, wetted, pelletized, sintered, etc.) being charged. Further, the design will include provisions for delivery of glass from the furnace in whatever manner (bottom drain, pour, vacuum, etc.) and at whatever rate is required by the forming mold and the process chosen for production of massive-glass pieces. The Owens-l'linois furnace used for producing the Cer-Vit telescope mirror blanks may represent a suitable design because the glass ceramic must be of very high quality for each application.

Molds

The mold has two functions: shaping of the glass, and acting as a heat interchanger. The mold, therefore, is the very heart of the forming process because it is the only piece of equipment directly in contact with the glass from the time that the charge is delivered until the formed piece is sufficiently rigid to maintain the shape and the planned dimensions when removed from the mold.

Aside from the problems of fabricating and finishing the large molds from suitable materials so that the glass will take the desired shape, dimensions, and as-formed surface finish, the major problem is the control of heat transfer between the mold and the massive piece of glass. There is a huge quant by of heat that must be removed in a carefully controlled manner.

The first portion of heat removed will cause the glass to become sufficiently rigid to maintain shape (forming). The second portion of heat is removed so that there will be minimal residual stress in the glass (annealing). The third portion of heat is removed to bring the glass to ambient temperature (cooling).

The mold must be brought up to operating temperature before the molten glass is introduced; otherwise, the glass will shrink away from the mold, not take the shape or finish intended, and not permit effective heat transfer between mold and glass to take place as planned. As the glass contacts the mold, the heat must be removed at controlled rates so that the temperature of the entire mold surface is kept as uniform as possible (approximately 300°F maximum variation), and at a temperature at which the glass will not stick to the mold. This degree of control is difficult to achieve, especially with massive sections of complex shape.

Release agents are commonly used to prevent the glass from sticking and have some effect on heat transfer; however, this is not well understood. This lack of understanding may be appreciated by the statement quoted from Tooley's <u>Handbook of Glass Manufacture</u>. (30)

"Along with the question of doping is the problem of these mold surfaces. Thickness of these oxide surfaces varies widely - from none almost up to one or so millimeter thickness. The working surfaces consist of some oxidized iron, a high amount of ferric oxide, some ferric phosphate, iron nitride, and with very little silica and small amounts of CaO and MgO. Some graphite is present especially when graphite or hydrocarbon oils have been used as lubricants or dopes. This picture really proves nothing other than that in most cases we do not form our glass against metals but against a surface so altered by heat and glass contact as to have little if any of the properties of the base metal."

The foregoing quotation raises a question as to how the mold surface for the large hemispheres or cylinders will be achieved and controlled if, in fact, the bare surface is not what is required. In iron-mold practice, the surface is acquired by repeated cycling of the mold in production.

Likewise, molds are brought up to optimum operating temperature by repeated contact with hot glass. It is doubtful that massive glass will be produced at rates and in quantities such that these customary industry practices can be followed. Other techniques will have to be developed.

In the fabrication of massive pieces of glass, regardless of composition, the mold as a controlled heat exchanger may require significant development effort. For this reason it is thought that molds, mold materials, and temperature-control systems for the various methods of forming should be high on the priority list for early investigation and selection.

Forming Methods

Of the forming methods described by Shand, ⁽³¹⁾those likely to be more practical for forming massive glass are: (1) pressing, (2) sagging, and (3) casting, or combinations thereof, with positive or negative pressure blowing as an assist.

Should the ultimate glass pieces be required initially or should the industry be encouraged to learn first the forming and handling techniques for the massive pieces? Certainly there is much to be said for phasing any large program, whether the phases run consecutively or concurrently. For forming and handling, this will require considerable effort to develop the methods, techniques, and specialized hardware to form, anneal, and handle large pieces of high-quality glass. This development is essential to the composition, surface strengthening, inspection, and joint design.

Pressing

Except for the size of the equipment required, pressing would ordinarily be high on the list of possible ways considered for forming hemispheres. This method of forming has the advantage of filling the mold relatively rapidly so that all mold surfaces are in contact with hot glass early in the heat-removal process, which, in turn, increases the possibility of controlling temperature differentials in the glass and the mold components, and of more effectively controlling the removal of heat uniformly from the glass. In pressing, the resulting intimate centact of glass and mold material further enhances the possible rate of heat removal.

Obviously, this method for forming massive glass requires specialized massive equipment. In all probability, the mold components would be permanent in nature, for they would have to withstand the large forces involved in the pressing operation. Further, the press machine will be huge in relation to known glass presses, and yet it must have relatively delicate and flexible control of action and thrust for the forming operation.

Such machines are not available presently in the glass industry. Presses capable of forming approximately 25-pound pieces exert approximately 80 tons of thrust (maximum). It is likely that a sizable design and development effort is required to scale up the press equipment to form a massi-e-glass piece weighing several tons.

We would expect the formed glass to be ejected by the mold valve if the female mold is one solid piece, or that the mold would be two or more pieces hinged so as to open from around the formed piece, leaving the glass supported on the mold bottom plate. In either instance, the glass would have had heat removed at least to the extent that the glass would not sag out of shape when the mold and glass were separated.

Sagging

An obvious advantage to forming a massive hemisphere by sagging or sag bending is the possibility of inspecting the intermediate sheet or blank of glass for quality before the forming operation is started. Then, when heat is applied to soften the blank, the total heat in the glass will be only a fraction of the heat content of a like amount of molten glass. As a result, the mold has much less heat to remove from the glass to allow the formed piece to be sufficiently rigid to be self-supporting when released from the mold.

A further possible advantage might be that, with only the force of gravity involved, it is unlikely that mold particles would be pressed into the surface of the glass and so generate failure origins. Still another advantage is that, without a solid mold portion forming the inside surface of the hemisphere, the glass can contract on cooling with less chance of placing it in tension.

To achieve these benefits, the sheet or blank of glass must be cast or rolled and then ground and polished, which entails the use of additional capital facilities. Those that exist are not necessarily available for producing special glass in small quantities. It appears that only minimal development rather than research is required prior to detailed design and construction. PPG has successfully sag-formed 56-inch-diameter hemispheres with 1.5-inch-thick walls of soda-lime glass.

Casting

Casting would appear to have a possible advantage over other methods of forming in that the molten charge would be directly introduced into the mold without requiring major equipment to prepare an intermediate product as for sagging, nor would it require a press capable of mechanically forcing

the glass into shape.

Because the casting method does not require the intermediate equipment (large presses or plate-glass lines), this process then lends itself to being set up in various parts of the country for multiple sources of supply if this should be required in the national effort.

Casting is the one of the three forming processes by which it is possible to form hatch openings directly in the hemisphere. Such an opening would need finishing but would not require the cutting operation, as would a sagged or pressed piece.

A problem that must be resolved is how to avoid putting the glass in tension as it contracts around the portion of the mold forming the interior of the piece. Possibly this member could be retracted gradually to compensate for the shrinking of the glass.

Relatively large pieces of glass, both crystallizable and noncrystallizable, have been cast successfully. The Corning mirror blank made 35 years ago is a prime example. Recently, Owens-Illinois has cast a 27-ton mirror blank of their crystallizable glass ceramic (Cer-Vit).

Protective Glass Coatings (for handling operations)

Pristine glass quickly loses a large percentage of its strength when the surface is damaged during normal handling in the industry. Damage is caused to some degree by contact with other glass, ware-handling mechanisms, packaging equipment, and anything that can possibly abrade the very susceptible unprotected fresh glass surface. To prevent or at least to minimize this surface damage, protective coatings are applied promptly to newly formed ware. A metallic film is applied to the hot glass soon after it is delivered from the forming mold. Later, when the glass has been cooled

to a relatively low temperature (in the range of room temperature to 350°F, depending on the material used), a further protective film is added. This is required before the glass is handled, inspected, or packed because it is easily damaged at this point in its processing.

What properties of coatings are required to provide this surface protection? Primarily, a coating is required that adheres to the surface, that can be applied uniformly, and that lubricates the ware surface so that the objects contacted slide over it easily. Such a coating does not in itself completely protect the glass from impact damage, but reduces impact damage to a minimum by vastly reducing the energy absorbed in a glancing blow. Secondarily, a coating with high puncture strength is needed to resist relatively heavy bearing pressures.

It is probable that massive-glass parts should be so protected but are the industry coatings adequate? Best puncture strengths achieved go to no more than 125 pounds. It is doubtful that such a coating would offer much protection to the massive (weight) glass with which we are concerned. A research program will, therefore, be required to define requirements and find or develop a suitable protective material.

Annealing (before strengthening)

When cooling of glass is uncontrolled, high residual stresses can result from excessive temperature gradients and therefore there is a greater possibility of failure. If the glass, as formed, has a temperature above the annealing range it must be cooled and, if below, it must be heated. The time for cooling or heating is then dependent on the temperature change required. With reference to Shand's $^{(31)}$ ideal schedule for commercial annealing of a soda-lime glass with expansion coefficient per degree C of 90 x 10^{-7} , we find that if cooling is applied to one surface or to both surfaces,

the time for annealing a half-inch thick section is the sum of the following times when the initial glass temperature is 440°C.

Time Duration in Minutes

		Heat & Cool Cne Side	Heat & Cool Two Sides
1.	Raise to 5°C above annealing temperature or 554°C	52	14
2.	Soak	30	30
3.	Lower temperature to 20°C below strain point	233	70
4.	Controlled cooling down 50°C to 434°C	84	25
5.	Rapid cooling to room temperature	- 145 544	<u>40</u> 179
		(9 hours, 10 minutes)	(2 hours, 59 minutes)

Similar calculations show that a 2.25-inch section heated and cooled on one surface will take nine days, and if heated and cooled from both sides will take almost three days for a commercial anneal. The annealing times for a 4.5-inch section will be 30 days or 9 days, depending on whether heating and cooling are applied on one or two surfaces.

A lower-expansion glass, of course, will require less time to arrive at a comparable annealing grade. Conversely, to improve the anneal will increase the time required.

Actually, considerable time will elapse between the start of the melt and the time that inspection of the resulting piece of glass can be completed to determine whether it is a piece of glass suitable for further processing or just scrap. Also, a significant amount of equipment will be tied up for each anneal, causing a low production rate and large capital investment.

Strengthening

Recognizing that glass fails in tension and that a!l but very carefully prepared specimens have surface flaws of some magnitude that act as stress concentrators, a way should be devised to prevent or eliminate these defects and then prevent recurrence. In the case of the large pieces of glass with which we are concerned, the foregoing appears to be impractical but may be required. However, when the best possible surface is achieved, all efforts should be made to preserve it.

Inability to achieve and maintain the perfect surface then points up the need to investigate means of preventing the surface from being placed in tension. The method used to date is to put the surface into compression so that the compressive prestress loading must be exceeded sufficiently by a larger tension-producing loading before failure can take place.

Of the three common ways of producing this surface compression - namely, thermal tempering, chemical tempering (above the annealing temperature), and chemical tempering (below the annealing temperature) - the first two are not applicable because distortion is likely to occur. The third method, or chemical strengthening (below the annealing temperature), leaves a lot to be desired because it requires a special composition suitable for ion exchange. Moreover, the process is time-consuming and to date only very shallow (.005" - .010") cases have been develored. If there are flaws deeper than this case, or if subsequent handling or processing produces flaws that penetrate this shallow a case, the glass is no stronger than the original (unstrengthened) glass. Deleterious effects of pre-existing defects can be minimized by a suitable acid etch before chemical strengthening. In addition, it will be necessary to develop the means of creating a relatively thick (0.1" or more) case without distorting

the piece. This requires a research and development effort of considerable importance to the whole project. It should receive a high priority, and could be done concurrently and relatively independently of other important phases.

Handling

The equipment and method for handling large pieces of glass must be carefully worked out; otherwise the surface will be damaged each time the piece is contacted. Equipment suitable for grasping, elevating, and turning the piece must be available at each location. which the glass is to be handled. Contacting materials must be such as will not mar the glass surface. Grasping forces and unit-bearing loads must be kept low to prevent scratching of the surface and chipping and spalling of the edges. A design program is required for the handling system.

Summary

The glass industry will have a large development program ahead to design and build suitable equipment and facilities, but even greater effort will be required to develop the techniques and train the personnel for the manufacture and handling of high-quality massive pieces of glass. These can be accomplished by several concurrent programs rather than sequential one. Primarily, the industry can develop many of the techniques by working with available glasses prior to the time the ideal composition and quality of glass are available.

The following recommendations are made for that part of the program that relates to the actual forming and subsequent processing of the massive glass pieces. It should be noted that some parts of the program could be started with very little delay and that several parts could go forward simultaneously, the parts being integrated at a later time.

- 1. The customer must project the requirement for massive-glass parts of various shapes, sizes, and production rates so that facilities can be planned realistically.
- 2. The customer must recognize the industry's need to develop equipment, techniques, and personnel to melt, form, anneal, strengthen, and handle massive pieces of glass. To this end, consideration should be given to the sort of pieces that could be produced and have some utility but yet would not have the critical performance specifications of glass for mannated vehicles. In ascending order of quality specification, massive-glass-forming projects should be assigned to industry as follows:
 - (a) General use without requirement for pressure loading or for being leak-proof
 - (b) Submerged use without man-rating but for pressure loading and to be leak-proof
 - (c) Submerged use with man-rating
- 3. In the long-term consideration of producing high-quality massive-glass parts, all the forming processes should be carefully considered. However, casting appears to have several advantages and thus should be thoroughly investigated initially. To this end, several suppliers should be programmed to investigate the casting of large relatively complex shapes. Production of castings would progress logically by:
 - (a) Using existing furnaces and glass compositions in current production
 - (b) Melting special glass of suitable composition and physical preparation of the batch in existing furnaces

(c) Melting special glass compositions with suitable batch preparation in furnaces specifically designed to produce the high-quality glass required by the program

In order to start such a program for production, the following prerequisite program must have been completed:

- (a) Determination of suitable mold material and mold design
- (b) Development of suitable handling equipment
- (c) Design and construction of suitable annealing furnaces
- 4. Very early in the production of massive-glass parts, there is a need to protect the surface of the glass from handling damage. Hence, a program for developing a protective coating and an application process should start at an early date. Such coating will not only be used on the glass as originally formed, but also will be reapplied as necessary after any operation that will disturb or destroy the protection. Thus, such coating must be compatible with the strengthening process and the final protective cladding, or be readily removable.
- 5. Recognizing that the glass part formed may take any one of several shapes (hemisphere, monolithic sphere, prolate spheroid, cylinder, etc.), equipment must be designed and constructed to accurately grind, polish, and measure:
 - (a) Flat joint surfaces
 - (b) Inside and outside contours
 - (c) Hatch and penetration openings

This program must be essentially completed before the basically formed glass parts can be assembled for test.

C. VEHICLE-DESIGN PROBLEMS

Introduction

Experimental work with glass shells, in the form of test models evaluated by being subjected to external hydropressurization, has demonstrated that glass structures can reach high compressive-stress levels under favorable conditions. Ultimate strengths of several hundred thousand pounds per square inch have been reported for small models. Whereas some experimental work has been done with cylindrical shapes, most of the recent effort has been with hollow spheres 10 inches or less in diameter.

The relatively low density of glass coupled with a high inherent compressive strength offers a potential strength/weight ratio higher than that of any structural metal. Thus, a pressure hull of massive glass would have the greatest buoyancy and payload potential.

The high inherent compressive strength of glass is much greater than the practical engineering strength that can be obtained with an actual model. Glass displays a very low tensile strength. Although the primary hydrostatic load on a submersible hull results in compressive wall stresses, there are always flaws, geometric imperfections from fabrication, and discontinuity stresses in the vicinity of penetrations and the assembly joints that produce tensile microstresses. When these stresses reach a critical magnitude, failure ensues while the average wall stress is compressive and an order of magnitude or two below the intrinsic ultimate strength.

The reason for the apparent low tensile strength of glass is attributed to another intrinsic quality, the inability of the material to yield locally in the vicinity of a sharp-edged flaw so that the local microstresses may be relieved, as occurs in the local plastic yielding of structural metals. Analogous problems were experienced in developmental rocket-motor cases

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(internal-pressurization loading) fabricated of ultra-high-strength steels (yield strength of 285,000 psi), where the critical flaw size in the shell wall under biaxial tension was determined to be smaller than could be detected prior to structural testing. Thus, if massive glass is to be used as a structural material, it will be necessary to prevent any critical flaws from being in the glass to minimize the occurrence of tensile or shear microstresses in the glass.

Since neither flaws nor tensile stresses (micro) can be prevented in a practical glass structure, the only possibility of developing a successful pressure hull with massive glass necessitates the alteration or treatment of the flaws to make them less critical, and/or a reduction in the intensity of tensile-stress components in the shell.

Reliability is an her major problem area if the program objective to man-rate a massive-glass pressure capsule is to be achieved. Reliability implies a failure-prediction capability. Failure points (critical loads) cannot be predicted "accurately" for glass structures. It is generally accepted that failures in glass always start at a flaw, and that glass surfaces always contain flaws. Consequently, the key to reliability may be in the identification and detection of all critical flaws.

Joints and penetrations, in addition to being major problems in themselves, aggravate other problems such as defects in the faying surfaces of the joints, or in the adjacent inner and outer surfaces of the shell. Assembly and access requirements necessitate one or more joints. Joints cannot be made accurately enough to assure a perfect fit and high local stresses result when the shell is loaded. To compensate, metal edging for the faying surfaces can be employed, but this introduces some new responses, and satisfactory thermal-expansion matching of the glass and the companion metal should be attained. To minimize joint stresses, relative

elastic behavior of the mating components must be carefully considered.

In addition to the structural aspects of joints and penetrations, a detail problem arises in the sealing against sea water of the joint's "common" boundary over the complete range of operational pressures from sea level (zero differential) to 13,500 psi (1.5 times maximum operating pressure for a 20,000-foot vehicle). Some elastomeric materials tend to "crystallize" at these higher pressures. However, seal compliance is particularly needed at low pressures (shallow depths). At the high pressures experienced during a deep dive, the seal must not be driven into the joint. Similarly, the joint must be protected against the intrusion of foreign solid material.

Structural support, equipment foundations, and other hard points ir roduce undesirable local loads externally and internally. Special design attention will be required to treat these unsolved problems.

Normal handling during fabrication and assembly, and normal service abuse could introduce scratches, chipped surfaces, and initiate cracks in the glass shell. In addition to using special care in handling and storage, protective "armor" coatings appear to be a utilitarian necessity. Repair of major defects does not appear to be feasible; however, refurbishing after a period of service may be possible if only minor damage has occurred. Such refurbishment might include chemical etching to blunt any sharp edge flaws, and repolishing, followed by new thermal and/or chemical treatments, and application of new protective coatings/armor. Also, sympathetic implosion of a hollow glass structural shell such as a pressure hull or buoyancy tank can be triggered by the collapse of an adjacent hollow shell. Adequate spacing of other methods of attenuating pressure transients should be considered in the design.

Procedures for Design of Hull and Appurtenances

Concept Selection and Justification

Basic Shape Selection

The selection of basic geometric shape is affected by many constraints, among which are structural performance, hydrodynamic considerations, internal arrangements, cost, materials, and producibility. The candidate shapes listed below each have major advantages in some of these areas, and disadvantages in others.

(a) Spheres (single)

The optimum shape of a pressure vessel from a structural point of view is a single monolithic sphere. If more than one material is used, multiple spheres can be advantageous.

A single sphere has obvious advantages when using massive glass as the structural material because it is relatively easy to form, and the two major orthogonal stresses "in-plane" (meriodional and equatorial) are equal in all areas except near penetrations or junctions. Since the single sphere is not hydrodynamically attractive, the pressure hull must be enveloped, or partially enveloped, by a hydrodynamically faired exostructure. The internal arrangement for personnel and equipment is more difficult to accomplish in a single sphere than in the other candidate shapes. Because its advantages outweigh its disadvantages, the single sphere probably will be the choice for the first full-scale massive-glass pressure hull of high structural efficiency.

(b) Spheres (multiple)

The use of multiple spheres, or a cluster of spheres, has several advantages over the single sphere, but it does present fabrication

problems not encountered in the single-sphere design. In relation to strength-te-weight ratio, multiple spheres utilizing a single material cannot be structurally as efficient as the single sphere. However, if a low-density, high-modulus material can be used as a reinforcement ring between the spheres, the strength-to-weight ratio of the multiple-sphere configuration can be designed to be lower than that of the single sphere. Model tests utilizing a ceramic (alumina) ring in a titanium bi-sphere successfully used this technique. (32)

In relation to both arrangement and hydrodynamics, the multiple spheres have advantages over the single spheres. Toroidal ballast tanks can be placed at the sphere intersections and the entire envelope can be hydrodynamically faired. Internal access from sphere to sphere is possible. It must be noted, however, that for structural efficiency the angle of intersection of the spheres should not be large.

(c) Cylinders with Hemi-Heads

One of the traditional pressure-vessel shapes has been a circular cylinder with hemispherical end closures. This shape has excellent arrangement characteristics and does not have to be hydrodynamically faired (except perhaps near the stern). Deep submersibles such as the ALUMINAUT have this shape. For structural efficiency, all the penetrations should be made in the hemi-heads. In metal hulls the cylindrical shells normally will be stiffened by internal frames. A major advantage of this configuration, which is not often recognized, is the fact that additional buoyancy can be obtained simply by extending or adding to the cylinder length. The need for additional bi syancy frequently occurs during the construction of small submersibles.

(d) Other Shapes

There are other appealing geometric shapes, but these introduce additional problems in design and in fabrication that may not be desirable to resolve concurrently with the development of a new application of material such as massive glass. The prolate spheroid is a good example. It has a higher scrength-to-weight ratio than a cylinder and only slightly less than the sphere. Its shape from a hydrodynamic and arrangement point of view is good.

Strength-to-Weight Ratios

The strength-to-weight ratio of the pressure hull is dependent upon the yield strength of the material, its elastic modulus, its density, the operating depth, and the design factor of safety. In its simplest form, it is merely the yield strength of the material divided by its density. This is misleading because the working stress levels will vary from material to material depending on the confidence factor the designer has in the material. Also, a common design practice (for certification) is to use two thirds of the yield strength as the allowable design strength.

A better criterion for the relative structural efficiency of pressure hulls having equal collapse depths is the weight-to-displacement ratio. This is the total weight of the fabricated hull divided by the weight of the water it displaces. Obviously, the lower the weight-to-displacement ratio is for any fixed design depth, the better the performance potential in terms of excess buoyancy (payload capability).

(a) Basic Hull Configurations (without penetrations;

It is simplest to discuss the weight-to-buoyancy ratio of unpenetrated hulls first, in order to illustrate the effect of geometry on this

performance parameter. For instance, the maximum stress (σ) in an unpenetrated sphere is:

$$\sigma_{\text{max}} = 3/2 \frac{Pb^3}{(b^3 - a^3)}$$

This sphere has a weight of

$$W = 4/3 \pi (b^3 - a^3) \rho_8$$

and a displacement of

$$D = 4/3 \pi b^3 \rho_w$$

where a and b are the internal and external radii respectively, $\rho_{\rm g}$ and $\rho_{\rm w}$ are the densities of sphere material and the water respectively, P = the external pressure, $\sigma_{\rm max}$ = maximum stress in an unpenetrated, idealized spherical shell. Using these values, the weight-to-displacement ratio is

$$W/D = 3/2 \left(\frac{\sigma_s}{\rho_w}\right) \frac{P}{\sigma_{max}}$$

This is the lowest value of any geometric shape. Bear in mind that in practical construction such factors as the lack of sphericity and penetrations will increase this ratio.

In comparison with spheres, the weight-to-displacement ratio of cylinders is 33 percent greater. Based on a maximum stress of

$$\sigma_{\text{max}} = \frac{2P b^2}{(b^2 - a^2)},$$

a weight of

$$W - \pi (b^2 - a^2) \ell_{\rho_c}$$

and a displacement of

$$D = \pi b^2 L_{\rho_c}$$

where ρ_{C} is the density of the cylinder material and \boldsymbol{t} is the length of the cylinder, the weight-to-displacement ratio is

$$W_{D} = 2 \left(\frac{o_{c}}{o_{w}} \right) \frac{P}{\sigma_{max}}$$

Similar types of calculations can be run on any candidate shape. Although they are idealized numbers, they provide a base line for the choice of geometry, and show the relative effectiveness of competing materials in the same hull design.

(b) Hull (with penetrations)

The penetrations in the pressure hulls affect the weight-todisplacement ratio in two basic ways:

- 1. They increase the stresses in the pressure hull, thereby reducing the allowable membrane stresses, which, in turn, increases the weight-to-displacement ratio.
- 2. The penetrations themselves usually weigh more than the hull material that they have replaced. The percentage increase is usually higher for the thinner shells used for shallow submergence than for thicker shells used for deeper submergence. General Dynamics' 2,000-foot STAR III submersible's penetrations increase the weight of the pressure hull by 15 percent. The ALUMINAUT, a 15,000-foot aluminum submarine, has penetrations only in the hemispherical heads. These penetrations increase the head weight by only 5 percent. For a pressure hull made of massive glass, the penetrations will be made of metals with higher densities than the glass. Therefore, the percentage increase in weight should be greater than

for the ALUMINAUT (>5 percent).

(c) Hull with Protective Coating

In addition to the added weight of the penetration inserts (build-up), a massive-glass pressure hull must be provided with external and internal protective coatings or armor. Presumably, the coating would be a low-density, transparent plastic material. Ideally, the coating's density would be no greater than that of water. Realistically, the coatings available today have densities around 20 percent higher than that of water. The protective coat on the inside of the glass could be thinner because the probability of damage is less; its weight is not compensated by displacement of an equal volume of sea water; whereas about 80 percent of the weight of the external coating will be compensated when submerged.

Types of Penetrations and Joints

It is obvious that the number of penetrations in a massive-glass hull should be kept at a minimum. Any failure occurring in the glass pressure hull most likely would initiate in the vicinity of a loaded edge, at an assembly joint, or between the glass and the penetrations. Other than evolving acceptable design allowable strength properties for the thick massive-glass hull material, design of the joints and penetrations is the most critical engineering and development aspect for a pressure vessel of this type.

(a) Connecting Ring

If a spherical hull is the chosen geometry, and if the glass is fabricated in either hemispherical or spherical segments, a connecting frame is necessary. The design of this structure greatly depends on the choice of material. Ideally, the material, presumably metal, would have the same bearing strength, elastic modulus, Poisson's ratio, and coefficient of thermal

expansion as the glass. The material also would have a high hardness. There are three candidate metals: (1) aluminum, (2) titanium, and (3) steel. The aluminum has the lowest density and the came elastic modulus as commercially available glass (not glass ceramic) but it is soft. Titanium, intermediate in density, has the same modulus as some glass ceramic and has adequate hardness. Steels have a higher modulus than glass and have adequate hardness, but high density. Obviously, a compromise is required.

(b) Hatches

Two general types of hatches are used in submersibles:

(1) seat type and (2) plug type. The seat-type hatch is easier to fabricate since very close tolerances are not required, but they are not as efficient structurally as plug-type hatches. In either case, a metallic hatch ring (seat) is required and the same type of problems encountered in the design of the equatorial or inter-segment connecting frames also will be encountered in the hatch design.

(c) Electrical Penetrations

The electrical penetrations used in a massive-glass hull will be similar to the standard ones used in metal hulls, but the location will be much more critical. Since they should not penetrate the glass material directly, they must be located in a hatch-reinforcement ring, the interconnecting metal ring, or some other metallic insert. The number of connectors should be minimized. Therefore, much of the electrical equipment should be outboard of the pressure hull in pressure-compensated chambers, and only the control system and life-support equipment with their necessary electrical leads located inboard.

(d) Other Penetrations

Other penetrations, such as viewports and piping penetrations,

may be necessary. Obviously, viewports will be necessary only if the glass material is not suitably transparent (such as most glass ceramics, or because of protective coatings). If viewports are necessary, they too will require metallic reinforcement rings similar to, but smaller than, hatch-penetration inserts. Piping penetrations should be avoided, particularly for deopsubmergence hulls. Usually, all the hydraulic systems can be located outboard of the pressure hull and can be controlled electrically from inside the pressure hull. If, for some special reason, such as a heat exchanger, piping penetrations are required, they would be located in metal insert areas.

Design Specifications

Assuming that the vehicle will be designed and built to Navy specifications, this documentation will be similar to NAVSHIPS 0900-028-2010. For structures using new shapes and materials, it will be necessary to prepare new specifications defining requirements of design safety, materials, tests, manufacturing techniques, and inspection methods and criteria for each particular component, as well as the assembled systems. These specifications will include a combination or portions of existing military, federal, and commercial specifications. The records and documentation necessary for certification must be defined at the initiation of the program.

Method of Analysis

(a) Elastic-Stress Analysis

To calculate the elastic stresses in shells of revolutions, numerous analyses are available. Usually, computer solutions are required for pressure vessels because the discontinuities at penetrations and reinforcements induce bending stresses. The analysis for constant thickness shells of revolution involves the solution of a pair of ordinary differential

equations, (33, 34) which can be solved by numerical integration.

The multisphere design also can be effectively employed. Usually, a multispherical hull is more amenable to hydrodynamic and arrangement considerations with little sactifice in structural efficiency. Again, many combinations of material can be used. A bi-sphere model could use a titanium hull with a ceramic reinforcement ring. (32) A massive-glass spherical hull could replace a portion of the titanium sphere and the sphere-sphere intersection region could be retained as titanium, or it could be designed using ceramic. Ceramics are candidates because of their high elastic modulus ($E \cong 50 \times 10^6 \text{ psi}^2$) and relatively low density ($\rho \cong .14 \text{ lb/in}^3$).

Cylindrical shells with hemispherical ends also can have many variations of geometry and materials. The particular problems involved with the use of massive glass in a cylindrical huli include: (1) elimination of stress amplification and concentration factors that induce tension, and (2) avoiding penetrations, other than in metal components of joints where the cylinder and heads intersect, or at the intersection of two cylinders.

(b) Stability Analysis

For a sphere, the collapse pressure due to elastic instability (buckling) can be approximated by:

$$P_c = \theta E \left(\frac{h}{R}\right)^2$$

where E = Young's modulus

h = average thickness over a critical arc length

R = local outer radius over a critical arc length.

Based on extensive model tests (both metallic and glass models) at the Naval Ship Research and Development Center, the recommended value for θ is:

$e \approx 0.84$ (for Poisr a's ratio = 0.3).

For machined hulls, the local radii usually can be kept to less than 1.05 times the nominal radius. For a glass hull, it should be possible to achieve a lower ratio if grinding and polishing of inner and outer surfaces is specified. Although the governing differential equations for the elastic behavior of massive-glass cylinders are the same as those for metallic cylinders, (34) the commonly used equations for calculating buckling pressures (35) have been verified experimentally only for ductile metallic cylinders. Because of the assumption that "lobar" modes form at the buckling pressure, the applicability of these equations for massive glass is doubtful.

(c) Cyclic Analysis

Massive-glass pressure hulls can be designed for elactic behavior and its elastic stability properties, but the behavior under cyclic loading is very difficult to analyze. Using the analytical methods developed from the areas of fracture mechanics and low-cycle fatigue, along with a great deal of test data, it may be possible to develop analytical are empirical methods of predicting the behavior of massive-glass pressure hulls under cyclic pressure loads.

(d) Impact Analysis

Since the glass hull will be protected by a protective plastic (transparent) coating, most of the unattenuated impact loads will be imparted to the glass through its penetrations. Therefore, the effect of dynamic loading of the connection ring, hatches, etc. must be analyzed as a basis for attenuating the shock loading before it is propagated to the glass hull. Standard shock analysis can be used, but the mechanical shock level that a glass hull can withstand will have to be determined by use of both the shock analysis and tests.

Fracture Mechanics

A fracture-mechanics study should be conducted to establish the mechanisms of crack initiation and propagation in the basic hull or massive-glass structure. Full-scale sections must be tested to evaluate effects of stress level and deflections on crack behavior. The effects of defects, stress concentrations and points of high local loading, must be evaluated.

Failure Modes and Mechanisms

Empirical studies of failure modes in highly stressed monolithic glass structures face the immediate challenge of leaving many, very small fragments that defy analysis as to fracture origin and propagation. It may prove useful to employ control instrumentation that can be set to unload the structure at the sensing of precursor events prior to gross failure. Glass structures with arrested cracks have been observed when tests were stopped and the components examined.

Triaxial-Stress Considerations

For practical considerations, the design-allowable tensile stress is virtually zero for glass. Consequently, it may be necessary to consider triaxial stress conditions in a practical structure where some flaws can be expected. As the shell thickness is increased in relation to the diameter of the pressure hull, stresses in the radial direction become important. The inner surface of the shell will be at lea-level pressure while the exterior surface is subjected to full sea pressure. The "biaxial" membrane stress probably will be five to six times greater than the hydrostatic pressure. Subsurface flaws may assume greater importance as operating stress levels are increased. Analytical methods may make it

possible to predict the level at which the mixture of triaxial stresses and particular flaws would cause failure.

Effects of Thermal Gradients and Differential Expansion across Joints

Under normal operating conditions, thermal gradients cannot be avoided. Similarly, different rates and amounts of expansion can be expected across joints whether the abutting materials are of the same type or have different expansion coefficients.

Analytical methods can be used to indicate the magnitude of "worst case" conditions of various candidate structures and materials in likely combinations. Possible additive effects of differential elastic deflections and differential thermal expansions also should be considered.

Thermal gradients occurring in a large multi-curved glass shell, resulting from an excursion from sea-level warmth to the cold of a deep dive, will contribute to deflections. This is particularly true in the region of the joints, and increases the stress intensity in the structural discontinuity, where it is least desired.

Different types of materials in contact present a greater likelihood of differential thermal deflections and the attendant undesirable stresses. The cushioning of the glass edge in an epoxy resin provides opportunity for some strain relief between the glass and its metal edge member. In summary, the analysis should be sufficiently detailed so that unacceptable thermal stresses do not occur in the design.

Effect of Geometric and Dimensional Tolerances and Tolerance Stacks

The analytical procedures used for highly stressed structures containing massive-glass components must include the effects of the unavoidable excursions from the ideal geometry. The best efforts applied in the

manufacture and assembly of practical structures always will result in a departure from perfection. The analytical acumen must be heightened considerably when dealing with structures containing brittle materials. These careful analytical considerations must extend beyond a single component to include the worst-case algebraic summations of possible tolerance accumulations for the complete structural system. Particular attention must be paid to the tolerance stacks that can occur at structural joints where edge-loading of the glass member may be affected critically.

Supporting Structures and Foundations

Many design details have been ignored in the structural test models fabricated to date. These are details of great importance to a manrated deep submersible. Even handling, a relatively simple matter for many components and test articles that can be moved by hand for manufacturing operations, inspection, assembly, test, and operational development, becomes a difficult matter when these operations must be accomplished with the aid of mechanical devices much less dexterous than the human hand. For a practical operating submarine with a glass pressure capsule, special provisions must be made in design to accommodate the peculiar characteristics of the glass material in regions of structural contact with other hardware components, both inboard and external. The external structure, in addition to supporting the static weight of the outfitted pressure capsule, must accommodate acceleration loadings that result from land, air, and sea transport as identified in a mission plan. Continuity between the exostructure and the pressure capsule introduces static and dynamic local loads in the glass shell necessitating careful design consideration.

Even without the added complications and mass of these other components, a particular design problem arises in attempting to retain, in relatively motionless juxtaposition, the major shell segments (hemispheres, cylinders, etc.), each weighing thousands of pounds. This detail is really another facet of the already complex problem of joint design. Attaching the pressure capsule to the exostructure and the internal structure within the pressure hull, present unique design problems when the major structural shell of the pressure hull is made of glass. Hull deflections with depth excursions must be prevented from introducing intolerable stresses in the glass members. Surface damage to the glass also must be prevented. Debris wedging into crevices could change a "clearance" to an interference fit and induce subsequent damage.

Design Refinement

Analysis and evaluation of test results may indicate a direction for design refinement and/or materials substitutions. In a sense, the opportunity for design refinement is one of the basic justifications for the testing of subscale models. Through such iterative processes it would be hoped that the design, construction, and test of full-scale pressure hulls could be accomplished at lower technical and economic risks. However, the alternative paths should be charted for sequences of sub-scale models followed by full-size prototypes, versus the option of using only full-size prototypes and the various cost/risk effectivities compared.

D. SCALE MODELS AND PROTOTYPES

A number of interesting structural concepts have been proposed and subscale models built. Three of these have been pressure-tested but the extent of the testing programs has varied with the different models. Each design has certain advantages and limitations. It is not intended to present any of these as the ideal, but each deserves careful consideration to evaluate its potential with respect to the over-all goal.

One design involves two transparent glass hemispheres with a machined titanium alloy ring at the equatorial joint. This design has a number of attractive features. Visibility is completely unrestricted and the finishing operations at the joint are relatively simple. However, penetrations constitute a very significant problem and access into the sphere must be accomplished by removal of one hemisphere (or through a hatch if provided in a hemisphere). When the glass-to-metal interface is disturbed by removal of a hemisphere, there is danger of damage with subsequent degradation in the reliability of the joint. On the other hand, design and fabrication of a hatch in a glass hemisphere also presents some problems that require study, development, and evaluation.

Another design consists of a titanium-alloy lattice into which 12 spherical pentagons of a glass ceramic are inserted to form a sphere. One or more glass segments can be replaced with titanium-alloy hatches to provide means of access and coupling with other modules to take advantage of the inherent flexibility of modular design. While this design with a glass fiber overwrap has zero visibility, a transparent glass hemisphere could be added to a hatch to provide an observation post. This complex design presents additional problems in machining and fit-up. There is also a question as to whether the much larger glass-to-metal interface surface area presents advantages over the minimum contact area between two glass bemispheres.

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A third design is basically a welded titanium-alloy bihemisphere configuration with a glass-ceramic hemisphere fitted to each end, forming an "hourglass" shape. Advantages accruing to this design include penetrations through metal only; access hatch(es) in the metal portion of the vessel; and the relatively simple finishing operations involved with hemispheres. This design, however, lacks the flexibility of modularity, and would tend to have a higher weight-to-displacement ratio because of the relatively higher percentage of titanium alloy than glass content in the structure.

From the three instances cited, it will be seen that there is no clear-cut advantage in one design to the exclusion of the others.

Subscale models are widely used in engineering studies since they are less expensive to fabricate than prototypes, and can be tested in smaller facilities. Since the testing can be done under closely controlled conditions, the models can be highly instrumented to provide engineering data concerning the response of the structure under load and the behavior of materials systems. Modifications of models can be effected at much lower costs than for full-size structures.

In an engineering-development test and scale-up program that would lead to the production of a man-rated deep-submersible vehicle capable of 2,000 dives to 20,000 feet, the testing of models approximately 18 inches in diameter would provide a useful starting point, although the program should adopt "full-scale" models as soon as basic design concepts have been developed and verified with the smaller models. The one-fifth size lends itself quite well to pressure-tank testing and instrumentation. After the joint designs have been optimized, a logical step in the testing program would be to subject each candidate design to the same cyclic pressure tests to determine which model(s) meets (meet) the 2,000-dive requirement. Assuming survival of at least one design when subjected to the cyclic testing, a duplicate

model should then be subjected to another series of cyclic tests in which the time under load would simulate actual operational conditions for the full-size vehicle. This would determine whether the successful designs are subject to structura! damage from delayed fracture mechanisms. At the completion of the cyclic loading tests, the models should be tested to destruction to determine whether the collapse depth capability had been compromised. It must be recognized that the successful completion of a scheduled series of tests on one model does not generate a high degree of confidence in that design, particularly if premature failure occurs. An iterative development effort must be accepted as inherent in this high-risk technical program. The next logical part of this first phase of a structural-glass program would be the fabrication of additional subscale models that could be used as instrumentation packages for the very deep oceanographic studies. The recent advances in electronics permit high-density packaging, which, when combined with the anticipated efficiency of glass structures, would provide a very significant advance in oceanographic instrumentation. The performance of these devices would help establish the reliability of the design and material and permit an evaluation of factors such as tolerance buildups, interfaces, finishes, handling requirements, protective coatings, types of defects induced by normal service abuse, etc.

Half-Scale Structures

The transition from the 18-inch models that have been discussed to a full-size 96-inch-diameter sphere is a major advance in the state of the art. Facility limitations and economics may justify an intermediate step. It has been established that both manufacturing and performance problems in 44-inch and 56-inch spheres are much more difficult than those experienced with 10-inch spheres. The responsible failure mechanism(s) has(have) not been evaluated fully. The preferred step toward full size

would appear to be a half-scale structure in which the metal-fabrication techniques and performance can be evaluated along with those of the thick section glass. The response to heat treatment of large thick glass sections in terms of final homogeneity needs to be better established, especially in the case of the glass-ceramic compositions. The effectiveness of a chemically strengthened layer in improving working strength of glass is probably independent of wall thickness, but this has not been established. In addition, it is not known whether the degraded performance of the heavy glass sections is strictly a function of the defect population or whether some other, more subtle, factors operate as in the case of heavy sections in metals.

The half-scale sphere thus would serve as a major stepping stone in the quest for a full-scale vessel. Both glass production and structure fabrication would be advanced. This structure also would provide indications of further scale-up problems, which then could be attacked. As an instrumentation package, the advantages of increased payload capability with resultant increase in diversity of payload, and operating time with larger power sources, are attractive features of this size.

Full-Scale Prototypes

As a practical approach to evaluation of the problem of producing a man-rated vehicle, the Committee has addressed itself to consideration of a "typical" deep-submergence hull with a nominal 96-inch diameter for 20,000-foot operating capability. (The glass-hull thickness would be about 4 inches for membrane stresses over 60,000 psi.) At present, industry has no capacity to melt, shape, heat treat, process and finish hemispheres of this diameter and thickness in quantity. Glass hemispheres of this size have not been built but no insurmountable problems are anticipated in the fabrication. Experience with glass in this thickness range in these

sizes is quite limited, and data on quality, reliability, and reproducibility are lacking. Therefore, it would be necessary to set up facilities for the fabrication of finished hemispheres in large numbers in the near future to supply an adequate quantity of test spheres on a timely basis before the man-rated glass submersible is designed and built.

The segmented-sphere design would require substantially less investment in new facilities. Each of the segments in a 96-inch sphere would have a maximum dimension of 60 inches. This is within the current capability of the glass industry, which has produced 56-inch hemispheres. Forming of the segments is simpler than forming of hemispheres but the final grinding and polishing to finished dimensions is more difficult and expensive.

The first step in the production of the full-scale pressure hulis would be the fabrication of a sufficiently large number of hemispherical or spherical segments to evaluate the reliability and reproducibility of these thick sections. This would require a very careful characterization of the glasses in regard to both properties and defects. Defects would be identified and observed during the testing phase.

The second step would require the static and cyclic pressure testing of selected full-scale engineering models containing as few defects as possible. This would be followed by tests on models containing "acceptable" defects to establish realistic design specifications and acceptance criteria. During testing, there should be continuous multi-channel monitoring of the elastic response of the test structures by use of strain gages, and the detection of flaw propagation and damage occurrence by acoustic and other means.

It is recognized that the testing of full-scale pressure hulls is more inconvenient than the testing of the subscale models. The number of facilities capable of handling and testing (to 10,000 to 15,000 psig) 96-inch

spheres is quite limited. The total cost of a cyclic test program that simulates expected lifetime operating conditions would be relatively high. In addition, the program approach could include full-size models used as unmanied instrument packages for oceanographic-data acquisition and other devices of interest to the Navy. The large physical size of the package permits installation of strain gages and other monitoring equipment with onboard recorders and transponders to evaluate the structural behavior of the pressure hull under operational conditions.

The correlation of engineering test data obtained on subscale models, with the actual performance of a full-size structure operating at great depths in the ocean, is difficult because of the unresolved questions concerning the properties and behavior of very large thick glass sections. However, since tests on smaller models can be conducted under closely controlled conditions with refined instrumentation, the engineering data are very useful in studying design details, materials compositions and properties, manufacturing processes, and structural response. As the test-model sizes are scaled-up, the economic factor becomes more significant. However, these larger models lend themselves more readily to such uses as instrumentation packages, thereby "paying their way" to some extent while still performing their primary function as engineering test equipment. Moreover, the greater similarity in size between the larger-scale models and the fullsize target vehicle produces experience and data that can be extrapolated with greater confidence to a full-size vehicle. The final steps in the development of a glass pressure hull require the fabrication, realistic testing under conditions that closely resemble those under which the man-rated vehicle would operate, and certification.

In summary, the subscale models can play a vital role in the early stages of engineering development and evaluation of design concepts,

and in the asseziament of structural responses of glass structures. Larger models, i.e., half-scale, are useful in studies of scale-up problems and for use as unmanned instrumentation packages or other devices. They can provide much useful data under actual operating conditions. The ultimate tests for man-rated vehicles will require full-size hulls. Because of the lead time required, the program for the production of full-size test vehicles should be started at about the same time that the subscale model work is undertaken. Real-life costs cannot be estimated at this point since production experience is so limited. The models fabricated and tested have been approximately 18 inches in diameter. Realistic cost estimates can be supplied by a summation of the estimates of the various participating potential contractors for program definition, design, integration, glass production, assembly, testing, etc.

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APPENDIX

CALCULATION OF ELASTIC PROPERTIES FROM COMPOSITION

Calculation of Young's Modul is

An empirical inethod of calculating Young's modulus has been developed by Phillips. (1) Applied to 73 simple and complex silicate glasses, agreement between calculated and observed values is better than ± 0.3 percent.

Calculation of Poisson's Rat o

W. B. Harsell, at Rutgers University, has recently measured Poisson's ratio for fused sil ca and obtained the same value, 0.163, as was previously obtained by Spinner. Thus we can have considerable confidence in this value.

For simple two-component alkali silicates, measurements by Harsell and by Jagdt ⁽⁴⁾ are in excellent agreement at 25 mole percent Na₂O and in quite good agreement at 33 to 34 mole percent Na₂O. This is shown in Figure 1. The values from Jagdt at 15 and 20 mole percent Na₂O seem somewhat too high. If we disregard these, the best fit straight line gives

$$v = .00163$$
 (mole percent SiO_2) + .00388 (mole percent Na_2O).

This is a very interesting result because the ratio, .00388/.00163 = 2.380, is very close to the ratio of the ionic radii, $Na^{2+}/Si^{4+} = 0.95/0.39 = 2.436$. If we assume that this is meaningful, we can calculate a value for K_2O of $0.0016 \times 1.38/0.39 = 0.005$. For CaO, the value is $0.0016 \times 1.00/03 = 0.0041$. The value for Al_2C_3 is $0.0016 \times 0.48/0.39 = 0.0020$.

We now assume that

$$v = C_1^{\rho_1} + C_2^{\rho_2} + \dots + C_n^{\rho_n}$$

where C_1 , ... C_n are coefficients for the respective oxides and ρ_1 , ρ_2 , ... ρ_n are the molar percentages for the corresponding oxides. We also assume

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that C_{SiO_2} and $C_{Al_2O_3}$ have constant values of 0.00163 and 0.0020, respectively, in all silicate glasses. The other coefficients C, on the contrary, are not constant but instead vary with the other oxides with which they are associated. In glass 38, for example, if the coefficients for SiO_2 and CaO have the values calculated from their ionic radii, the correct value for v can be obtained only if $C_{Na_2O} = 0.00315$, a value considerably less than that calculated from its radius. It appears that the coefficient for Na_2O depends on the amount of CaO with which it is associated. The same seems to be true for K_2O , as shown in Figure 2, and the dependence appears to be on RO in general, not on CaO alone.

Glass 65 begins to give some insight into the behavior of B₂O₃. There is no RO present and thus Na₂O and K₂O must have their maximum values. To calculate a v, which matches Spinner's observation, the coefficient for B2O3 must be slightly negative. In glass 71, on the other hand, and again with no RO present, the coefficient for B₂O₂ must be quite strongly positive. It appears that ${^C}_{B_2O_3}$ is not governed primarily by the amount of ${^{SiO}}_2$ present since both glasses 65 and 71 have large amounts of that oxide. One obvious difference is that glass 65 contains more K₂O than Na₂O whereas the reverse is true for glass 71. However, this is not the only consideration because glass 58 also contains more K₂O than Na₂O but, regardless of the value assigned to the 1.0 mole percent ZnC that is present, the coefficient for B₂O₃ must here be at least slightly positive. An empirical expression that seems to satisfy the requirements for all three glasses is shown in Figure 3. The integer "1" in both numerator and denominator is simply a device to prevent the expression from becoming zero or going to infinity. It is evident that, unlike several other oxides, the coefficient for B₂O₃ does not depend primarily on its ionic radius.

Glass 67 makes it obvious that the coefficient for CaO is not invariant. The coefficients for NO_2 , $\mathrm{Na}_2\mathrm{O}$, $\mathrm{K}_2\mathrm{O}_3$ having already been established, it is evident that the coefficient for CaO must be much less than 0.0041. The value is evidently not dependent on $\mathrm{R}_2\mathrm{O}$ because that is nearly the same as in glass 38. It appears to depend on $\mathrm{SiO}_2 + \mathrm{Al}_2\mathrm{O}_3 + \mathrm{f}(\mathrm{B}_2\mathrm{O}_3)$ as shown on Figure 4. The value of $\underline{\mathrm{f}}$ is given by Figure 5 and is the same as was used by Phillips (1) in calculating Young's modulus. Belief in the trend shown for CaO is reinforced by glass 66. Here the coefficients for the other oxides are already well established, so for CaO it must of necessity be zero.

Glass 54 gives us a coefficient for BaO because the behavior of the other oxides is already known. This glass shows that $C_{BaO} = 0.0058$, exactly the value calculated from its ionic radius. This is of great help because, using glass 55, we can calculate $C_{ZnO} = 0.0007$ at $SiO_2 + Al_2O_3 + f(B_2O_3) = 59.3$ mole percent. If this value is connected by a straight line with the much higher coefficient for ZnO in glass 58, glasses 56, 61, and 63 fall nicely on this line. In all of these, the coefficient for BaO remains at 0.0058. To maintain the linear relationship for ZnO, it becomes necessary for the BaO coefficients to decrease for glasses 62, 64, 59, and 60. However, this was the general behavior encountered in calculating Young's modulus and so is not unexpected. It would seem that the coefficient for ZnO, like that for B_2O_3 , does not depend on its fonic radius.

The method for calculating the effect of PbO is much less satisfactory than for the other oxides. Glasses 42 and 43, and 45-51, all contain substantial amounts of this oxide. Five of these glasses contain both K_2O and Na_2O , and for these the values seem to vary from one glass to another in a very erratic way. The only relationship which seems to predict C_{PbO} accurately for these glasses is shown in Figure 6. $C_{\text{PbO}} = x/y$, where \underline{x} is the value from the $SiO_2 + Al_2O_3 + f$ (B_2O_3) curve and \underline{y} is the value from

the R₂O curve.

Four of the complex glasses also contain PbO. For glass 57, the curves of Figure 6 predict $C_{\mathrm{PbO}}=0.008$ and this high value turns out to be exactly what is needed to give this glass the correct ν value. Note that this glass contains 3.0 mole percent ZnO. In glasses 61, 62, and 59, there are larger amounts of ZnO together with BaO. It quickly becomes evident that for these glasses C_{PbO} cannot have the full value calculated from Figure 6. In fact, in glass 61, C_{PbO} must be zero. This can be accomplished if C_{PbO} behaves as in Figure 7.

Although the procedure outlined here is largely empirical, the calculated values of Poisson's ratio agree within ± 1 percent with the observations of Spinner and Harsell for the 28 glasses they measured. Young's modulus can also be computed and with even greater accuracy. We are thus in quite a good position to "hand tailor" glass compositions so that $v_g/E_g = v_m/E_m$ at glass-metal interfaces, at least for normal glasses substantially free of exotic ingredients. Hopefully, some of these glasses also will meet the other requirements of ease of melting, good glass quality, high light transmission, good chemical durability, etc.

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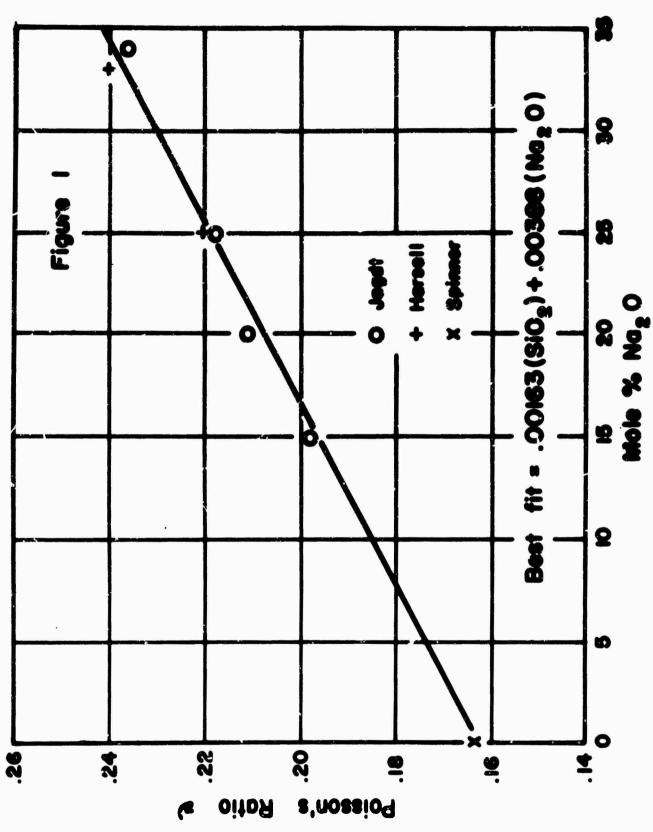
996		Component	Oxddes	(mole %)							Potsson's Ratio	Ratio		
Number*	Reference	SiO ₂ (a)	Na O	К ₂ 0	M203	B ₂ 03	CaO	Pbo	Ba	ZnO	Observed	Calculated	Difference(s) (b)	ê
38	3	7.1	14.5	١.	,	•	14.5	,	,	,	. 221	. 221	0.0	1
39	က	57.3	14.2	•	•	14.3	14.2	•	•	•	. 242	. 242	0.0	
42	ဗ	61.7	ı	2.9	t	•	•	35.4	:	E	. 230	. 230	0.0	
43	က	64.6	•	3.8	•	1	•	31.6	4	1	. 228	. 228	0.0	
	က	8.99	1	5.3	•	•	,	27.8	,	•	. 213	. 213	0.0	
46	က	68.2	•	9.9	•	1	•	25.2	•	ē	. 200	200	0.0	
47	က	69.2	1.1	g , g	•	•	•	22.8	•	•	. 215	. 215	0.0	
48	က	71.1	4.5	5.9		•	•	18.8	,	ı	.212	.212	0.0	
49	က	69.6	7.3	5.8	:	ı	,	17.5	•	1	. 227	. 227	0.0	
20	က	72	3.2	8.	•	•	1	16.4	•	•	. 239	. 238	0.0	
51	က	76.8	9.0	8.7	•	•	•	13.6	0.3	1	. 231	. 231	0.0	
54	က	54.5	ı	•	2.4	12, 9	6.7	•	23.5	1	. 262	. 260	8.0-	
55	က	55.6	1	•	3.7	8.4	3,5	0.1	24.3	4.4	. 288	. 259	* .	
56	ဗ	56.7	0.3	0.4	4.3	5.6	,	9.0	28.0	6.1	. 260	. 262	æ.≎	
57	က	77.7	6.5	9.1	,	•	ı	3.1	1	3.0	. 242	. 242	0.0	
58	က	71.5	7.8	8.2	ı	11.5		•	•	1.0	205	204	ج ب	
59	က	68.9	2.0	7.2		•	•	6.9	7.1	4.8	. 224	. 224	0.0	
09	က	71.6	3.8	7.9	1	3.5	1	•	9.5	3.7	. 228	. 228	0.0	
61	က	62.4	3.0	5.2	•	5.1	•	2.0	14.8	7.5	. 232	. 233	₹.0+	
62	က	66.8	,	7.3	ı	ı	•	9.8	7.7	8.7	. 221	. 231	0.0	
63	ဗ	63.5	1.1	5.9	1.2	5,5		1	15.5	7.3	. 246	. 245	9	
64	3	66.2	0.5	6.0	•	4.2		•	16.1	7.0	. 241	. 241	0.0	
65	က	74.0	8.1	10.0	1	7.9		•	•	•	. 207	. 207	0.0	
99	က	75.2	14.7	3.3	:	4.4	2.4	•	1	1	. 210	. 210	0.0	
67	က	73.2	13.7	1.6	•	1.3	10.2	•	ŧ	•	7 02.	204	0.0	
7.1	က	83.1	3.8	0.3	1,3	11.5	•	1	•	1	700	. 199	9.0	
74	က	100. C	1	•		1	•	•	•	•	. 163		ı	
75	~	100.0	1	•	•	•	1	•	•	•	. 163	•	•	
92	8	75.0	25.0	•	•	•	1	•	ı	1	. 219	1	•	
77	4	75.0	25.0	•	ı	ı	1	:	•	1	.216	1	i	
78	83	67.0	33.0	•	•	•	1	ı	1	1	. 240	i	•	
79	4	66.0	34.0	ı	ı	ı	ı	1	1	•	. 236	•	í	

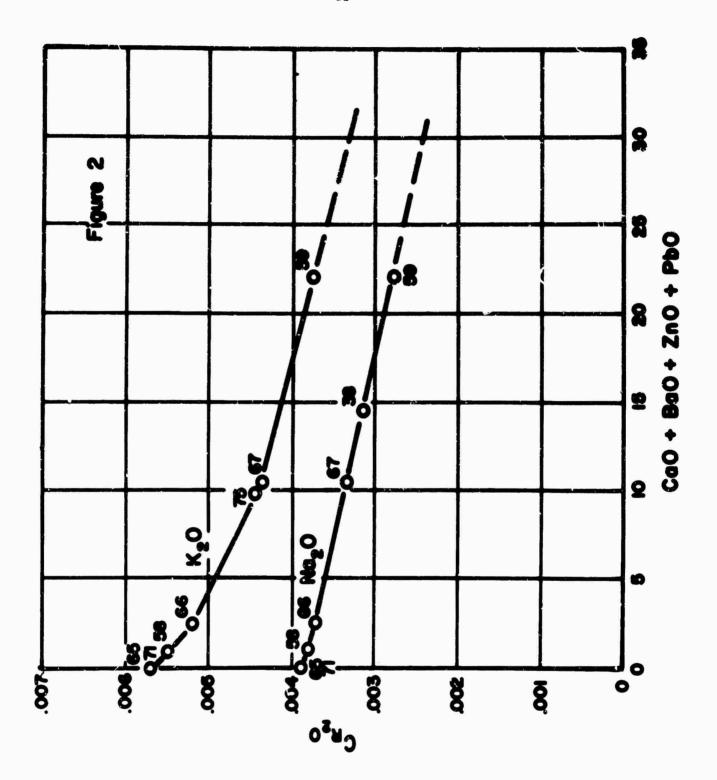
* Glass numbers 38-67 are same as in paper by Phillips, reference 1.

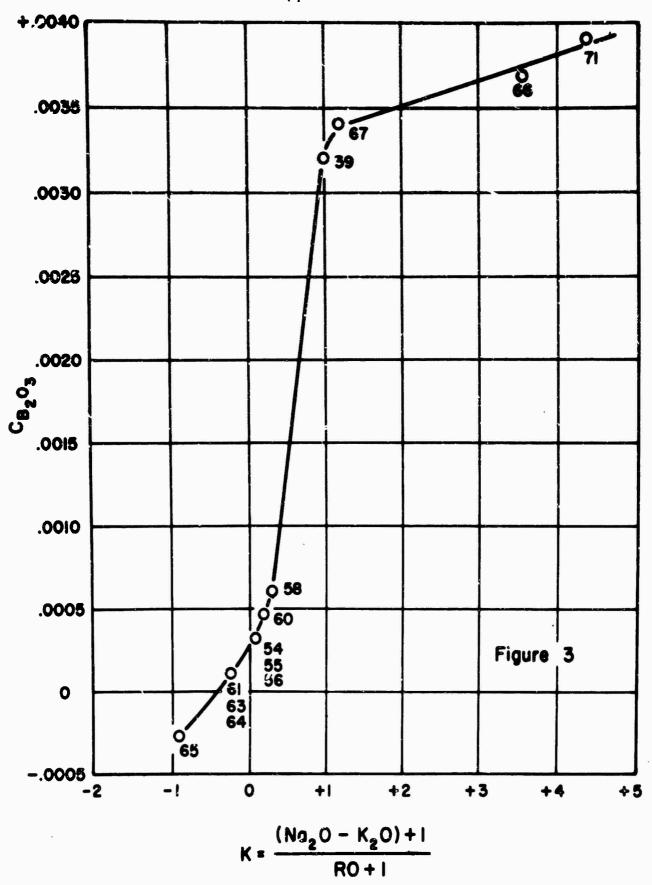
⁽a) Minor ingredients - $As_2^O_3$, $Sb_2^O_3$, C1 - included in SIO_2

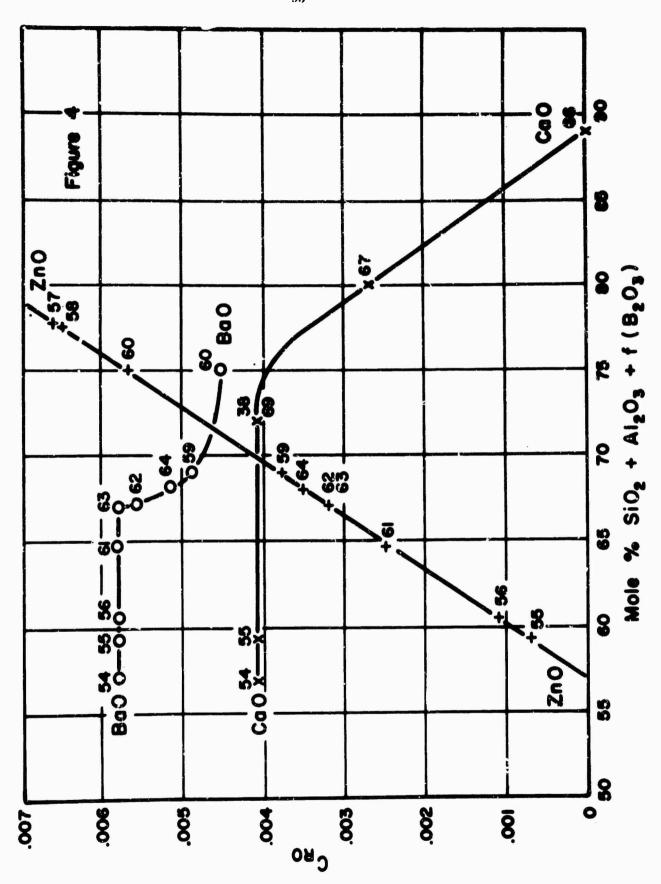
⁽b) Difference to nearest 0.1%

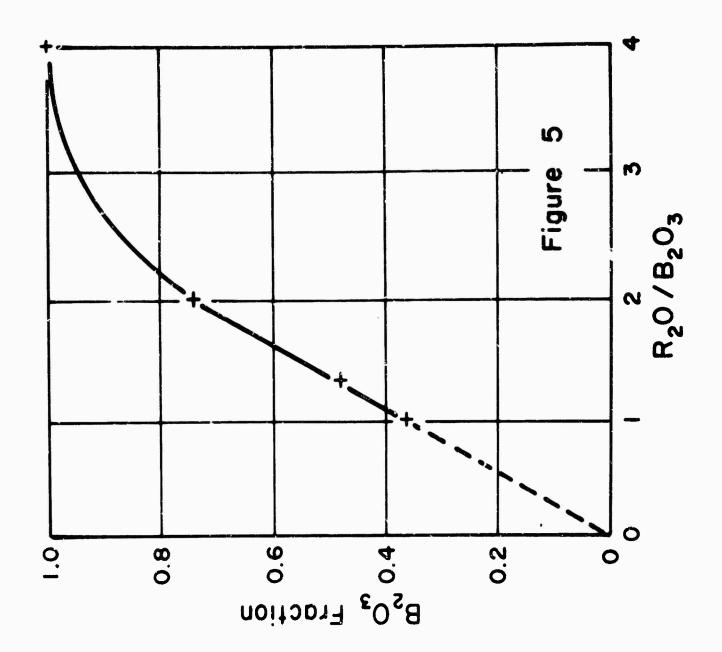


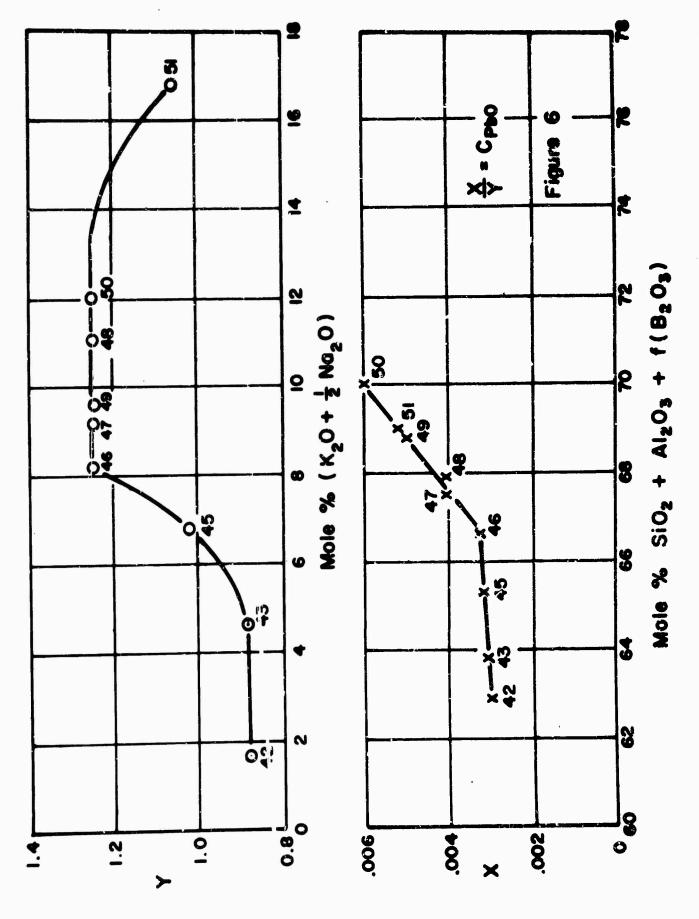


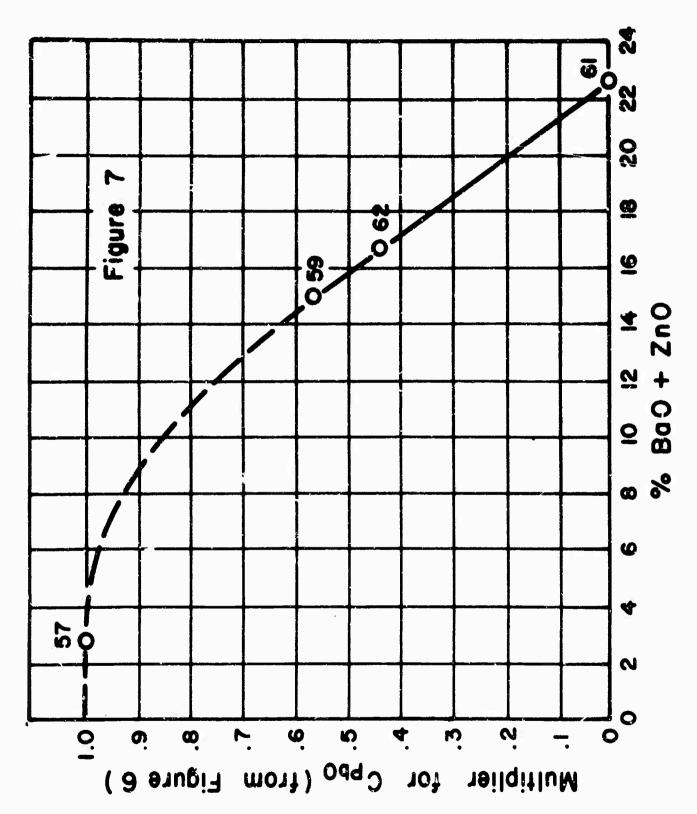












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11. SUPPLEMENTARY NOTES 12. SPONSORING MILITARY ACTIVITY Office of the Department of Defense								
None Office of the Department of Defense Research and Engineering, The Pentagon, Washington, D. C.								
Massive glass has potential as a structural material for a variety of high efficiency, deep ocean applications. However, neither the existing data on massive glass nor current industrial production capability are adequate for the task. This is especially true in producing a man-rated glass pressure hull by a target date of 1980.								
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THE NATIONAL ACADEMY OF SCIENCES is a private, honorary organization of more than 700 scientists and engineers elected on the basis of outstanding contributions to knowledge. Established by a Congressional Act of Incorporation signed by Abraham Lincoln on March 3, 1863, and supported by private and public funds, the Academy works to further science and its use for the general welfare by bringing together the most qualified individuals to deal with scientific and technological problems of broad significance.

Under the terms of its Congressional charter, the Academy is also called upon to act as official—yet independent advisor to the Federal Government in any matter of science and technology. This provision accounts for the close ties that have always existed between the Academy and the Government, although the Academy is not a governmental agency and its activities are not II ited to those on behalf of the Government.

THE NATIONAL ACADEMY OF ENGINEERING was established on December 5, 1964. On that date the Council of the National Academy of Sciences, under the authority of its Act of Incorporation, adopted Articles of Organization bringing the National Academy of Engineering into being, independent and autonomous in its organization and the election of its members, and closely coordinated with the National Academy of Sciences in its advisory activities. The two Academies join in the furtherance of science and engineering and share the responsibility of advising the Federal Government, upon request, on any subject of science or technology.

THE NATIONAL RESEARCH COUNCIL was organized as an agency of the National Academy of Sciences in 1916, at the request of President Wilson, to enable the broad community of U. S. scientists and engineers to associate their efforts with the limited membership of the Academy in service to science and the nation. Its members, who receive their appointments from the President of the National Acade ny of Sciences, are drawn from academic, industrial and governmental organizations throughout the country. The National Research Council serves both Academies in the discharge of their responsibilities.

Supported by private and public contributions, grants, and contracts, and voluntary contributions of time and effort by several thousand of the nation's leading scientists and engineers, the Academies and their Research Council thus work to serve the national interest, to foster the sound development of science and engineering, and to promote their effective application for the benefit of society.

THE DIVISION OF ENGINEERING is one of the eight major Divisions into which the National Research Council is organized for the conduct of its work. Its membership includes representatives of the nation's leading technical societies as well as a number of members-at-large. Its Chairman is appointed by the Council of the Academy of Sciences upon nomination by the Council of the Academy of Engineering.

THE NATIONAL MATERIALS ADVISORY BOARD is a urit of the Division of Engineering of the National Research Council. Organized in 1951 as the Metallurgical Advisory Board, through a series of changes and expansion of scope, it became the Materials Advisory Board and, in January 1969, the National Materials Advisory Board. In consonance with the scope of the two Academies, the general purpose of the Board is the advancement of materials science and engineering, in the national interest. The Board fulfills its purpose by: providing advice and assistance, on request, to government agencies and to private organizations on matters of materials science and technology affecting the national interest; focusing attention on the materials aspects of national problems and opportunities, both technical and nontechnical in nature, and making appropriate recommendations as to the solution of such problems and the exploitation of these opportunities; performing studies and critical analyses on materials problems of a national scope, recommending approaches to the solution of these problems, and providing continuing guidance in the implementation of resuring activities; identifying problems in the interactions of materials disciplines with other technical functions, and defining approaches for the effective utilization of materials technologies; cooperating in the development of advanced educational concepts and approaches in the materials disciplines; communicating and disseminating information on Board activities and related national concerns; promoting cooperation with and among the materials related professional societies; maintaining an awareness of trends and significant advances in materials technology, in order to call attention to opportunities and possible roadblocks, and their implications for other fields, and recognizing and promoting the development and application of advanced concepts in materials and materials processes.